# REMEDIAL INVESTIGATION AND FEASIBILITY STUDY WORK PLAN CORNELL-DUBILIER ELECTRONICS SUPERFUND SITE OPERABLE UNIT NO. 3 (OU-3) GROUNDWATER

## ATTACHMENT A FIELD SAMPLING PLAN (FSP) AND QUALITY ASSURANCE PROJECT PLAN (QAPP)

**Prepared for:**

**Dana Corporation**

**Prepared by:**

**HydroQual, Inc.**
**Mahwah, New Jersey**

**Environ Corporation**
**Princeton, New Jersey**

**de maximis, inc.**
**Clinton, New Jersey**

**February 2006**
**DANA.001.001.02.0B**

HydroQual

Environmental
Engineers & Scientists

# ATTACHMENT A

# FIELD SAMPLING PLAN (FSP) AND QUALITY ASSURANCE PROJECT PLAN (QAPP)

# FIELD SAMPLING PLAN
# QUALITY ASSURANCE PROJECT PLAN

## OPERABLE UNIT NO. 3
## CORNELL-DUBILIER ELECTRONICS SUPERFUND SITE
## SOUTH PLAINFIELD, NEW JERSEY

**Prepared for:**

**Dana Corporation**

**Prepared by:**

**HydroQual, Inc.**
**Mahwah, New Jersey**

**Environ International**
**Princeton, New Jersey**

**de maximis, inc.**
**Clinton, New Jersey**

**February 2006**

# A PROJECT MANAGEMENT

## A1 Title and Approval Sheet

**Document Title:** Field Sampling Plan/Quality Assurance Project Plan
Operable Unit No. 3 (OU-3), Cornell-Dubilier Electronics Superfund Site

**Lead Organization:** U.S. Environmental Protection Agency

**Effective Date:** February 2006

**Lead Organization, US Environmental Protection Agency:**

Peter Mannino/Remedial Project Manager — Date

**Project Coordinator: de maximis, inc.**

William J. Lee — Date

**Supervising Contractor: HydroQual, Inc.**

Principal in Charge – Gary J. DiPippo, P.E. — Date

Project Manager/QA Officer - Timothy R. Roeper, P.G. — Date

**Subcontractor (Soil Gas, Air and Risk Assessment): ENVIRON Corporation**

Principal in Charge - Ranjit Machado — Date

**Analytical Laboratories: Severn Trent Laboratories (STL)**

Michael J. Urban, STL Edison Lab Manager — Date

Janae McCloud, STL Edison Project Manager — Date

# A2 Table of Contents and Document Control Format

# Table of Contents and Document Control Format (Continued)

Appendix A - Groundwater SOP's

Groundwater Sampling SOP
Color-Tec Field Screening SOP
Discrete Interval Packer Sampling SOP
Packer Pressure Testing SOP
Borehole Geophysical Testing SOP
Water FLUTe Liner System Installation SOP
Equipment Decontamination SOP
Rock Core collection for Laboratory Testing SOP
Monitoring Well Construction SOP
Laboratory SOPs

Appendix B – Soil Vapor and Indoor Air SOP's

U.S. Environmental Protection Agency (EPA). January 1999. Compendium Method *TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specialty-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)* from the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.* Second Edition.(http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf) Center for Environmental Research Information. Office of Research and Development. Cincinnati, OH

USEPA. 2002. *Standard Operating Procedure (SOP) for Installation of Sub-Slab Vapor Probes and Sampling Using EPA Method TO-15 to Support Vapor Intrusion Investigations.*

USEPA. 1996. *Environmental Response Team (ERT) Standard Operating Procedure (SOP) #2042 Soil Gas Sampling; June.*

U.S. EPA. July *1995. Environmental Response Team (ERT) Standard Operating Procedure (SOP) #1704: SUMMA Canister Sampling.*

Sentinel Mobile Laboratory SOP

Example *Questionnaire,*
Example *Canister Field Data Sheet*
Example *Chain of Custody* record
Example *Access Agreement*
*Resident Instructions*

# LIST OF TABLES

# LIST OF FIGURES

## A3 Distribution List

This distribution list will be updated and signed once agency approval has been obtained.

| FSP/QAPP Recipients | Title | Organization | Date of Receipt | Telephone Number | Revision Number |
|---|---|---|---|---|---|
| Peter Mannino | Remedial Project Manager | U.S. Environmental Protection Agency | | (212) 637-4395 | |
| William J. Lee | Project Coordinator | de maximis, Inc. | | (908) 735-9315 | |
| Bruce Thompson | Project Coordinator | de maximis, Inc. | | (860) 298 0541 | |
| Gary J. DiPippo, P.E. | Principal in Charge | HydroQual, Inc. | | (201) 529-5151 | |
| Timothy R. Roeper, P.G. | Project Manager/QA Officer | HydroQual, Inc. | | (201) 529-5151 | |
| Ranjit Machado | Principal in Charge | Environ Corporation | | (609)-243-9871 | |
| Christopher Buzgo | Project Manager | Environ Corporation | | (609)-243-9871 | |
| Michael J. Urban | Laboratory Manager | STL Edison | | (732) 549-3900 | |
| Janae McCloud | Project Manager | STL Edison | | (732) 593-2554 | |
| Maureen Migliorini | Data Validator | HydroQual, Inc. | | (201) 529-5151 | |
| | | | | | |
| | | | | | |
| | | | | | |

# A4 Project/Task Organization and Schedule

The organizations and key individuals involved with the OU3 investigation are illustrated in Figure A4-1. The roles and responsibilities of the identified companies and individuals are as follows:

**United States Environmental Protection Agency (USEPA)**

Mr. Peter Mannino will act as the Remedial Project Manager on behalf of USEPA. In this role, Mr. Mannino will be the point of contact with the Federal government for the transfer of information including progress reports, analytical data, reports, etc. Mr. Mannino, on behalf of USEPA, will be responsible for the review of the data and submittals developed under this Work Plan for conformance with the provisions of the Settlement Agreement and the approved Work Plan.

USEPA's Region 2 Quality Assurance Reviewer, to be designated by USEPA, will be responsible for the review and approval of the FSP/QAPP associated with this project.

**de maximis, inc.**

Mr. William J. Lee will act as the Project Coordinator on behalf of Dana Corporation. In this role, Mr. Lee will be responsible for overall project management and coordination among Dana Corporation, USEPA, and HydroQual, Inc. In addition, Mr. Lee will have overall responsibility for implementing the work in accordance with the approved Work Plan and the Settlement Agreement.

**HydroQual, Inc.**

HydroQual, Inc. will act on behalf of the Dana Corporation as the Contractor performing the OU 3 RI/FS work for the site and will perform, direct, and oversee implementation of the investigative and engineering work called for in the Work Plan.

Mr. Gary J. DiPippo, P.E. is the Project Mangerand will also serve as the Task Manager for the FS-related tasks. Mr. DiPippo will have overall responsibility for maintaining communication with the Project Coordinator as well as for implementing the project in accordance with the approved Work Plan.

Mr. Timothy R. Roeper, P.G. will serve as the Project Manager for the RI and in that role will also function as the QA Officer. In this role, Mr. Roeper will be responsible for implementing the QA procedures defined in this FSP/QAPP, and with coordinating with the Project Coordinator, the laboratory's QA Manager and additional subcontractors as necessary. Mr. Roeper will manage implementation of the work plan activities for the OU-3 investigation.

**ENVIRON Corporation**

ENVIRON Corporation will serve as a subcontractor to HydroQual, assisting with the risk assessment and soil vapor intrusion aspects of the work. Mr. Ranjit Machado, P.E. will be the Principal in Charge for ENVIRON and will have overall responsibility for communication and coordination with the HydroQual Project Manager and for performance of the work in accordance with the approved Work Plan and the provisions of the Settlement Agreement. Mr. Christopher Buzgo will serve as the Task Manager for the vapor intrusion work. Mr. Adam Johnston will serve as the Task Manager for the risk assessment work.

**Severn Trent Laboratories (STL)**

STL Edison will provide the laboratory analytical services associated with the OU-3 groundwater investigation. Ms. Janae McCloud is STL Edison's Project Manager for the work. Ms. McCloud will manage the day-to-day activities associated with the analytical program for the RI. Mr. Carl Armbruster will serve as the QA Manager for the laboratory and in this capacity he will implement QA procedures defined in the QAPP and in the laboratory's SOPs. Ms. McCloud will report to Ann Gladwell, the STL Laboratory

Director. Mr. Michael Urban will be STL's Technical Director. Ms. Gladwell and Mr. Urban will have overall responsibility for the laboratory performance.

### Technical Advisory Team

A Technical Advisory Team will provide input to the project team for state-of-the-science technical support and review of strategic and key technical matters. The Technical Advisory Team will consist of Dr. John A. Cherry and Dr. Beth L. Parker of the University of Waterloo for DNAPL, fractured rock, and matrix diffusion issues; Robert D. Mutch Jr. and William G. Soukup of HydroQual, Inc. for fractured rock, DNAPL, matrix diffusion, and groundwater modeling issues; and Dr. Joseph V. Rodricks of ENVIRON for risk assessment and indoor air issues.

The anticipated schedule is provided in Section 5.0 of the Work Plan.

## A5 Problem Definition/Background

In accordance with the Statement of Work (SOW), the objectives of this Work Plan are to:

- Through the implementation of an RI, assess the nature and extent of groundwater impacts and whether such impacts, if any, pose a potential threat to human health, welfare or the environment;
- As a part of the RI, assess the potential for vapor migration to indoor air, and whether such impacts, if any, pose a potential threat to human health,; and
- Through an FS, evaluate alternatives for remedial actions that may be required as a result of identified impacts.

This FSP/QAPP is designed to achieve these objectives with respect to the collection of data. Details regarding the historical site operations, past investigations, etc. are provided in the Work Plan.

# A6 Project/Task Description

The tasks to be implemented under this FSP/QAPP, as part of the OU-3 investigation, consist of well drilling and installation, aquifer testing, groundwater sampling, water level monitoring, soil gas sampling, and indoor air sampling (sub-slab and indoor air). The methodologies used to collect these data are presented herein and maps illustrating sample locations are presented in the Work Plan.

# A7 Quality Objectives and Criteria for Measurement Data

## A7.1 Project Quality Objectives

Data generated will be reviewed by the USEPA. The precision, accuracy, representativeness, comparability, completeness, and sensitivity of the sampling and analytical procedures must be adequate to allow the data to be used to determine and confirm the presence of constituents in groundwater above their respective MCLs or New Jersey Groundwater Quality Standards (NJGWQS), or in the absence of established MCLs or NJGWQS, at Risk Based Concentrations. In the event that a detection limit is greater than the criteria referenced above, the associated constituent will be included for further evaluation as a possible Contaminant of Potential Concern (COPC) in the risk assessment. To assess the appropriateness of including each constituent, the risk assessment will consider the likelihood that a constituent is present below the detection limit (e.g. daughter product, historical information) and the weight of evidence on the toxicity of the constituent (e.g., Class A carcinogens will be given high priority for inclusion as a COPC). Finally, the data will be used to assess the extent of impact and aid in selecting a remedy.

For soil gas, the results must be comparable to soil gas screening levels (SGSL's) provided in the NJDEP October 2005 Vapor Intrusion Guidance document. Residential and nonresidential levels of concern for carcinogens represent a $10^{-6}$ (one in one million) excess lifetime cancer risk or the practical quantitation limit (PQL). Non-cancer levels of concern represent a hazard quotient of 1 or the PQL. The nonresidential levels of concern are based

on exposure factors for adult workers. Details on the derivation of SGSLs are contained in the NJDEP Vapor Intrusion Guidance. The levels of concern for indoor air samples are based upon the indoor air screening levels (IASL) provided in the NJDEP October 2005 Vapor Guidance.

With respect to the field analysis of groundwater samples to aid in decision-making regarding the installation of intermediate casings and the depth of investigation, the field method must be capable of routinely detecting the presence of chlorinated volatile organics above 5 to 10 ppb. In addition, the methodology must be semi-quantitative to allow for a determination of relative concentrations with depth. The method must be easily and costs effectively implemented in the field and provide reliable, decision quality data.

Field screening of soil gas samples must be capable of achieving detection limits for chlorinated solvents between 2 and 5 ppbv. Detection limits at this level are typically lower than the screening levels referenced above. The method must provide quantitative and reliable data on a "real time" basis to facilitate both field decisions and determine the potential for vapor migration to indoor air.

Groundwater samples will be analyzed for the following: Target Compound List (TCL) volatile organic compounds (VOCs), TCL semivolatile organic compounds (SVOCs), Target Analyte List (TAL) metals (including cyanide), Target Compound List Pesticides and PCBs. A subset of samples may be analyzed for PCB Congeners, Dioxin/Furan, and reductive dechlorination indicator parameters consisting of nitrate/nitrate, chloride, sulfate, phosphate, carbonate/bicarbonate, carbon dioxide, methane, propane, ethene/ethane, volatile fatty acids, TKN, and ammonium.

Field screening of groundwater samples will detect the presence and semi-quantitative concentration of total chlorinated solvents. The determination of individual constituents will not be required. Field analysis of soil vapor samples will be for PCE, TCE, Cis-1,2-DCE, 1,2,4-trichlorobenzene, and vinyl chloride. The method will report quantitative values for the individual constituents at detection limits between 2 and 5 ppbv. Soil gas and indoor

air samples sent for laboratory analysis will be analyzed for the full TO-15 list of volatile organics.

The parameters for analysis, and their respective action levels, and analytical method detection limits are presented in Table A7-1.

## A7.2 Measurement Performance Criteria

Measurement performance criteria determine the acceptable performance levels for the quality elements to be monitored. Tables A7-2 and A7-3 describe the measurement performance criteria in detail.

Additional performance criteria include data representativeness, data completeness, and data comparability. Data representativeness is a qualitative parameter that expresses the degree to which sample data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point or an environmental condition. This measurement is most dependent upon the proper design of the sampling program and proper laboratory protocol. Therefore, data representativeness will be satisfied by following established SOP's for sample collection, storage, handling, analysis and reporting. Data completeness is expressed as the percentage of valid data obtained from the measurement system. For data to be considered valid, it must meet the acceptable criteria including accuracy and precision, as well as other criteria specified by the analytical method used. Therefore, data points critical to the sampling program in terms of completeness will be validated as provided in Section D. Finally data comparability requires that samples be consistently collected, handled, analyzed and reported so that results obtained from multiple sampling events can be compared. Adherence to standardized analytical methods and quality control procedures will generate comparable data.

## A8 Special Training Requirements and Certification

The groundwater field sampling teams will be trained in the collection and shipment of environmental samples to the selected laboratory. At least one individual will be trained in the operation and recording of data obtained from the Color-Tec field screening method. For field analysis of soil gas samples, at least one individual will be trained in the calibration and operation of the field GC/MS. Training will be accomplished through familiarization with the equipment, manufactures operations manual, the SOP's included with the FSP/QAPP, the analysis of "practice" samples and prior experience. No specialized certification of the sampling team is required beyond 40-hour OSHA training. The analytical laboratory will be certified for the analysis of samples in the Sate of New Jersey.

## A9 Documentation and Records

Final copies of the RI/FS Work Plan and associated documents (e.g. HASP, FSP/QAPP) will be distributed to the individuals listed in Section A-3 upon approval by the USEPA. Revised
documents will also be distributed as needed. Field and analytical data will be generated, maintained, and retained as described in Section B10.

## TABLE A7-1

## ANALYTICAL PARAMETERS, ACTION LEVELS, AND METHOD DETECTION LIMITS 2006

| Analyte (Analytical Method) | Action Level (MCL) | NJ Ground Water Quality Criteria[1] | MDL/IDL |
|---|---|---|---|
| **Inorganics (SW-846 6010B/7470A)** | **mg/L** | **µg/L** | **mg/L** |
| Aluminum | 0.2 (SMCL) | 200 | 0.077 |
| Antimony | 0.006 | 6 | 4.86 [2] |
| Arsenic | 0.10 | 3 | 2.40 [2] |
| Barium | 2 | 2,000 | 0.002 |
| Beryllium | 0.004 | 1 | 0.0003 |
| Cadmium | 0.005 | 4 | 0.001 |
| Calcium | | | 0.075 |
| Chromium | 0.1 | 70 | 0.003 |
| Cobalt | | | 0.004 |
| Copper | 1.3 (TT) | 1,300 | 0.005 |
| Iron | 0.3 (SMCL) | 300 | 0.047 |
| Lead | 0.015 (TT) | 5 | 0.003 |
| Magnesium | | | 0.070 |
| Manganese | 0.05 (SMCL) | 50 | 0.003 |
| Mercury | 0.002 | 2 | 0.0001 |
| Nickel | 0.1 (remanded) | 100 | 0.004 |
| Potassium | | | 0.315 |
| Selenium | 0.05 | 40 | 0.005 |
| Silver | 0.1 (SMCL) | 40 | 0.003 |
| Sodium | | 50,000 | 0.396 |
| Thallium | 0.002 | 2 | 1.78 [2] |
| Vanadium | | | 0.005 |
| Zinc | 5 (SMCL) | 2,000 | 0.006 |
| Cyanide | 0.2 | 100 | 0.002 |

## TABLE A7-1

## ANALYTICAL PARAMETERS, ACTION LEVELS, AND METHOD DETECTION LIMITS 2006

| Analyte (Analytical Method) | Action Level (MCL) | NJ Ground Water Quality Criteria[1] | MDL/IDL |
|---|---|---|---|
| **Volatile Organics (624)** | µg/L | µg/L | µg/L |
| 1,1,1-Trichloroethane | 200 | 30 | 0.34 |
| 1,1,2,2-Tetrachloroethane | | 1 | 0.34 |
| 1,1,2-Trichloroethane | 5 | 3 | 0.33 |
| 1,1-Dichloroethane | | 50 | 0.32 |
| 1,1-Dichloroethene | 7 | 1 | 0.35 |
| 1,2-Dichloroethane | 5 | 2 | 0.29 |
| cis-1,2-Dichloroethene | 70 | 70 | 0.43 |
| trans-1,2-Dichloroethene | 100 | 100 | 0.43 |
| 1,2-Dichloropropane | 5 | 1 | 0.29 |
| 2-Butanone | | | 0.94 |
| 2-Hexanone | | | 0.52 |
| 4-Methyl-2-pentanone | | | 0.52 |
| Acetone | | 6,000 | 1.26 |
| Benzene | 5 | 1 | 0.33 |
| Bromodichloromethane | | 1 | 0.32 |
| Bromoform | | 4 | 0.22 |
| Bromomethane | | | 0.32 |
| Carbon disulfide | | 700 | 0.34 |
| Carbon tetrachloride | 5 | 1 | 0.31 |
| Chlorobenzene | 100 | 50 | 0.45 |
| Chloroethane | | | 0.24 |
| Chloroform | | 70 | 0.52 |
| Chloromethane | | | 0.29 |
| cis-1,3-Dichloropropene | | 1 | 0.24 |
| Dibromochloromethane | | 1 | 0.27 |
| Ethylbenzene | 700 | 700 | 0.46 |
| Methylene chloride | | 3 | 0.51 |
| Styrene | 100 | 100 | 0.39 |
| Tetrachloroethene | 5 | 1 | 0.45 |
| Toluene | 1,000 | 1,000 | 0.40 |
| trans-1,3-Dichloropropene | | 1 | 0.24 |
| Trichloroethene | 5 | 1 | 0.37 |
| Vinyl chloride | 2 | 1 | 0.28 |
| Xylenes (total) | 10,000 | 2,000 | 1.11 |

## TABLE A7-1

## ANALYTICAL PARAMETERS, ACTION LEVELS, AND METHOD DETECTION LIMITS 2006

| Analyte (Analytical Method) | Action Level (MCL) | NJ Ground Water Quality Criteria[1] | MDL/IDL |
|---|---|---|---|
| **Semi-Volatile Organics (625)** | mg/L | µg/L | µg/L |
| Phenol | | 2,000 | 0.61 |
| 2-Chlorophenol | | 40 | 1.08 |
| 2-Methylphenol | | | 1.07 |
| 4-Methylphenol | | | 1.15 |
| 2-Nitrophenol | | | 1.59 |
| 2,4-Dimethylphenol | | | 2.02 |
| 2,4-Dichlorophenol | | 20 | 1.44 |
| 4-Chloro-3-methylphenol | | | 1.64 |
| 2,4,6-Trichlorophenol | | 20 | 2.18 |
| 2,4,5-Trichlorophenol | | 700 | 1.19 |
| 2,4-Dinitrophenol | | 40 | 0.88 |
| 4-Nitrophenol | | | 0.87 |
| 4,6-Dinitro-2methylphenol | | | 1.23 |
| Pentachlorophenol | 0.001 | 0.3 | 2.08 |
| bis(2-chloroethyl)ether | | 7 | 0.87 |
| 1,3-Dichlorobenzene | | 600 | 0.96 |
| 1,4-Dichlorobenzene | | 75 | 0.90 |
| 1,2-Dichlorobenzene | | 600 | 1.09 |
| bis(2-chloroisopropyl)ether | | 300 | 0.85 |
| N-Nitroso-di-n-propylamine | | 10 | 0.74 |
| Hexachloroethane | | 7 | 0.90 |
| Nitrobenzene | | 6 | 0.96 |
| Isophorone | | 40 | 0.94 |
| bis(2-chloroethoxy)methane | | | 0.86 |
| 1,2,4-Trichlorobenzene | | 9 | 0.91 |
| Naphthalene | | 300 | 0.21 |
| 4-Chloroaniline | | 30 | 0.68 |
| Hexachlorobutadiene | | 1 | 0.60 |
| 2-Methylnaphthalene | | | 1.12 |
| Hexachlorocyclopentadiene | 0.05 | 40 | 0.63 |
| 2-Chloronaphthalene | | 600 | 1.07 |
| 2-Nitroaniline | | | 1.00 |
| Dimethylphthalate | | | 1.09 |
| Acenaphthylene | | | 0.12 |
| 2,6-Dinitrotoluene | | | 1.28 |
| 3-Nitroanaline | | | 0.66 |
| Acenaphthene | | 400 | 0.13 |
| Dibenzofuran | | | 0.91 |
| 2,4-Dinitrotoluene | | 10 | 1.14 |
| Diethylphthalate | | 6,000 | 0.78 |
| 4-Chlorophenyl-phenylether | | | 1.05 |
| Fluorene | | 300 | 0.16 |
| 4-Nitroaniline | | | 0.63 |
| N-nitrosodiphenylamine | | 10 | 1.06 |
| 4-Bromophenyl-phenylether | | | 1.20 |
| Hexachlorobenzene | 0.001 | 0.02 | 0.32 |
| Phenanthrene | | | 0.08 |

## TABLE A7-1

## ANALYTICAL PARAMETERS, ACTION LEVELS, AND METHOD DETECTION LIMITS 2006

| Analyte (Analytical Method) | Action Level (MCL) | NJ Ground Water Quality Criteria[1] | MDL/IDL |
|---|---|---|---|
| Anthracene | | 2,000 | 0.12 |
| Carbazole | | | 1.08 |
| Di-n-butylphthalate | | | 1.01 |
| Fluoranthene | | 300 | 0.13 |
| Pyrene | | 200 | 0.13 |
| Butylbenzylphthalate | | 100 | 1.05 |
| 3,3-Dichlorobenzidene | | 30 | 4.92 |
| Benzo(a)anthracene | | 0.1 | 0.17 |
| Chrysene | | | 0.19 |
| bis(2-Ethylhexyl)phthalate | 0.006 | 3 | 1.04 |
| Di-n-octylphthalate | | 100 | 1.00 |
| Benzo(b)fluoranthene | | | 0.13 |
| Benzo(k)fluoranthene | | | 0.09 |
| Benzo(a)pyrene | 0.0002 | | 0.06 |
| Indeno(1,2,3-cd)pyrene | | | 0.08 |
| Dibenzo(a,h)anthracene | | | 0.10 |
| Benzo(g,h,i)perylene | | | 0.09 |

## TABLE A7-1

## ANALYTICAL PARAMETERS, ACTION LEVELS, AND METHOD DETECTION LIMITS 2006

| Analyte (Analytical Method) | Action Level (MCL) | NJ Ground Water Quality Criteria[1] | MDL/IDL |
|---|---|---|---|
| **General Chemistry** | **mg/L** | **µg/L** | **mg/L** |
| Nitrate/Nitrite | 10/1 | 10,000 | 0.013 |
| Chloride | 250 (SMCL) | 250,000 | 0.766 |
| Sulfate | 250 (SMCL) | 250,000 | 0.614 |
| Carbonate/Bicarbonate | | | 0.788 |
| Methane | | | 0.00008 |
| Ethene | | | 0.00012 |
| Ethane | | | 0.000143 |
| Volatile Fatty Acids | | | |
| Lactic Acid | | | 1 (RL) |
| Propionic Acid | | | 1 (RL) |
| Butyric Acid | | | 1 (RL) |
| Acetic Acid | | | 1 (RL) |
| Pyruvic Acid | | | 1 (RL) |
| Formic Acid | | | 1 (RL) |
| Phosphate (Total) | | | 0.0035 |
| TKN | | | 0.098 |
| Ammonium | | | 0.034 |

[1] - Higher Values of Practical Quantitation Level (PQL) and Ground Water Quality Criterion
[2] - Will be analyzed using GFAA instrumentation
TT - Treatment Technique
SMCL - Secondary Maximum Contaminant Level
RL - Reporting Limit

## TABLE A7-1

## ANALYTICAL PARAMETERS, ACTION LEVELS, AND METHOD DETECTION LIMITS 2006

| Analyte (Analytical Method) | Residential | | Nonresidential | | MDL Field (8260B) | MDL Laboratory (TO-15) |
|---|---|---|---|---|---|---|
| **Chlorinated VOC's in Soil Gas** | **µg/m³** | **ppbv** | **µg/m³** | **ppbv** | **ppbv** | **ppbv** |
| cis-1,2-DCE | 1,800 | 460 | 2,600 | 640 | 2 - 5 | ≤ 0.5 |
| PCE | 34 | 5 | 36 | 5 | 2 - 5 | ≤ 0.5 |
| TCE | 27 | 5 | 27 | 5 | 2 - 5 | ≤ 0.5 |
| 1,2,4-Trichlorobenzene | 180 | 25 | 260 | 34 | 2 - 5 | ≤ 0.5 |
| Vinyl Chloride | 13 | 5 | 48 | 19 | 2 - 5 | ≤ 0.5 |
| **Chlorinated VOC's in Indoor Air** | | | | | | |
| cis-1,2-DCE | 36 | 9 | 51 | 13 | 2 - 5 | ≤ 0.5 |
| PCE | 3 | 0.5 | 3 | 0.5 | 2 - 5 | ≤ 0.5 |
| TCE | 3 | 0.5 | 3 | 0.5 | 2 - 5 | ≤ 0.5 |
| 1,2,4-Trichlorobenzene | 6 | 1 | 9 | 2 | 2 - 5 | ≤ 0.5 |
| Vinyl Chloride | 1 | 0.5 | 1 | 0.5 | 2 - 5 | ≤ 0.5 |

Note : The above list includes only the site constituents of concern. Laboratory analysis will report the full TO-15 analyte list. Detected constituents will be compared to the most current screening criteria. See the SOP for TO-15 in Appendix B for reporting limits for all reported compounds.

**TABLE A7-2**

**MEASUREMENT PERFORMANCE CRITERIA**

| Parameter | Analytical Methods/SOP | Data Quality Indicators (DQIs) | Measurement Performance Criteria | Activity Used to Assess Measurement Performance |
|---|---|---|---|---|
| TCL VOC | 624/TO-15 (water/air) | Precision | Within Limits indicated on Table A7-3 | Field Duplicates, MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < MDL | Rinsate Blanks, Trip Blanks, Method Blanks |
| TCL SVOC | 625 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates, MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < MDL | Rinsate Blanks, Trip Blanks, Method Blanks |
| TAL Metals | 6010B, 7470A | Precision | Within Limits indicated on Table A7-3 | Field Duplicates MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |

**TABLE A7-2 (CONTINUED)**

**MEASUREMENT PERFORMANCE CRITERIA**

| Parameter | Analytical Methods/SOP | Data Quality Indicators (DQIs) | Measurement Performance Criteria | Activity Used to Assess Measurement Performance |
|---|---|---|---|---|
| | | Accuracy – Contamination | < RL | Rinsate Blanks, Method Blanks |
| Nitrate/Nitrite | EPA 353.2 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < RL | Rinsate Blanks, Method Blanks |
| Chloride | SM4500-Cl B | Precision | Within Limits indicated on Table A7-3 | Field Duplicates, MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < RL | Rinsate Blanks, Method Blanks |
| PCBs | 8082 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates MS/MSD |

**TABLE A7-2 (CONTINUED)**

**MEASUREMENT PERFORMANCE CRITERIA**

| Parameter | Analytical Methods/SOP | Data Quality Indicators (DQIs) | Measurement Performance Criteria | Activity Used to Assess Measurement Performance |
|---|---|---|---|---|
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < RL | Rinsate Blanks, Method Blanks |
| Sulfate | EPA375.4 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates, MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < RL | Rinsate Blanks, Method Blanks |
| Carbonate/Bicarbonate | SM2320B | Precision | Within Limits indicated on Table A7-3 | Field Duplicates NO MS/MSD DONE!! |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | Laboratory Control Samples |
| | | Accuracy – Contamination | < RL | Rinsate Blanks, Method Blanks |

**TABLE A7-2 (CONTINUED)**

**MEASUREMENT PERFORMANCE CRITERIA**

| Parameter | Analytical Methods/SOP | Data Quality Indicators (DQIs) | Measurement Performance Criteria | Activity Used to Assess Measurement Performance |
|---|---|---|---|---|
| Methane, Ethane, Ethene | 3810 Modified | Precision | Within Limits indicated on Table A7-3 | Field Duplicates MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | <RL | Rinsate Blanks, Method Blanks |
| Volatile Fatty Acids | Dionex proprietary method | Precision | Within Limits indicated on Table 7-3 | MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table 7-2 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < QL | Rinsate Blanks, Trip Blanks, Method Blanks Field Duplicates |
| Phosphate (Total) | EPA365.2 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates, MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |

**TABLE A7-2 (CONTINUED)**

**MEASUREMENT PERFORMANCE CRITERIA**

| Parameter | Analytical Methods/SOP | Data Quality Indicators (DQIs) | Measurement Performance Criteria | Activity Used to Assess Measurement Performance |
|---|---|---|---|---|
| | | Accuracy – Contamination | <RL | Rinsate Blanks, Method Blanks |
| TKN | EPA351.2 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | < RL | Rinsate Blanks,Method Blanks |
| Ammonium | EPA350.2+350.1 | Precision | Within Limits indicated on Table A7-3 | Field Duplicates MS/MSD |
| | | Accuracy – Laboratory | Within Limits indicated on Table A7-3 | MS/MSD, Laboratory Control Samples |
| | | Accuracy – Contamination | <RL | Rinsate Blanks,Method Blanks |

## TABLE A7-3

## ANALYTICAL LABORATORY DATA QUALITY OBJECTIVES FOR PRECISION AND ACCURACY

| Parameter | QC Compounds | MS/MSD Precision (RPD) % | Blanks | LCS & MS/MSD Accuracy (%R) | Surrogate Accuracy (%R) |
|---|---|---|---|---|---|
| Volatile Organics (Water) | 1,1,1-Trichloroethane | 35 | <MDL | 52-162 | NA |
| | 1,1,2,2-Tetrachloroethane | 35 | <MDL | 46-157 | NA |
| | 1,1,2-Trichloroethane | 35 | <MDL | 52-150 | NA |
| | 1,1-Dichloroethane | 35 | <MDL | 59-155 | NA |
| | 1,1-Dichloroethene | 35 | <MDL | 0-234 | NA |
| | 1,2-Dichloroethane | 35 | <MDL | 49-155 | NA |
| | trans-1,2-Dichloroethene | 35 | <MDL | 54-156 | NA |
| | 1,2-Dichloropropane | 35 | <MDL | 0-210 | NA |
| | Benzene | 35 | <MDL | 37-151 | NA |
| | Bromodichloromethane | 35 | <MDL | 35-155 | NA |
| | Bromoform | 35 | <MDL | 45-169 | NA |
| | Bromomethane | 35 | <MDL | 0-242 | NA |
| | Carbon tetrachloride | 35 | <MDL | 70-140 | NA |
| | Chlorobenzene | 35 | <MDL | 37-160 | NA |
| | Chloroethane | 35 | <MDL | 14-230 | NA |
| | Chloroform | 35 | <MDL | 51-138 | NA |
| | Chloromethane | 35 | <MDL | 0-273 | NA |
| | cis-1,3-Dichloropropene | 35 | <MDL | 0-227 | NA |
| | Dibromochloromethane | 35 | <MDL | 53-149 | NA |
| | Ethylbenzene | 35 | <MDL | 37-162 | NA |
| | Methylene chloride | 35 | <MDL | 0-221 | NA |
| | Tetrachloroethene | 35 | <MDL | 64-148 | NA |
| | Toluene | 35 | <MDL | 47-150 | NA |
| | trans-1,3-Dichloropropene | 35 | <MDL | 17-183 | NA |
| | Trichloroethene | 35 | <MDL | 71-157 | NA |

## TABLE A7-3

## ANALYTICAL LABORATORY DATA QUALITY OBJECTIVES FOR PRECISION AND ACCURACY

| Parameter | QC Compounds | MS/MSD Precision (RPD) % | Blanks | LCS & MS/MSD Accuracy (%R) | Surrogate Accuracy (%R) |
|---|---|---|---|---|---|
| | Vinyl chloride | 35 | <MDL | 0-251 | NA |
| | 1,2-Dichloroethane-d4 | NA | NA | NA | 69-131 |
| | Toluene-d8 | NA | NA | NA | 69-131 |
| Volatile Organics (Air) | All Analytes | 25 | <PQL | +/-30 | NA |
| | Bromofluorobenzene | NA | NA | NA | 67-128 |
| Semi Volatile Organics | Phenol | 40 | <MDL | 0-84 | NA |
| | 2-Chlorophenol | 40 | <MDL | 57-97 | NA |
| | 2-Nitrophenol | 40 | <MDL | 61-109 | NA |
| | 2,4-Dimethylphenol | 40 | <MDL | 56-93 | NA |
| | 2,4-Dichlorophenol | 40 | <MDL | 63-109 | NA |
| | 4-Chloro-3-methylphenol | 40 | <MDL | 64-112 | NA |
| | 2,4,6-Trichlorophenol | 40 | <MDL | 61-116 | NA |
| | 2,4-Dinitrophenol | 40 | <MDL | 20-124 | NA |
| | 4-Nitrophenol | 40 | <MDL | 7-54 | NA |
| | 4,6-Dinitro-2methylphenol | 40 | <MDL | 47-137 | NA |
| | Pentachlorophenol | 40 | <MDL | 48-124 | NA |
| | bis(2-chloroethyl)ether | 40 | <MDL | 64-103 | NA |
| | 1,3-Dichlorobenzene | 40 | <MDL | 41-84 | NA |
| | 1,4-Dichlorobenzene | 40 | <MDL | 38-95 | NA |
| | 1,2-Dichlorobenzene | 40 | <MDL | 45-88 | NA |
| | bis(2-chloroisopropyl)ether | 40 | <MDL | 65-109 | NA |
| | N-Nitroso-di-n-propylamine | 40 | <MDL | 68-121 | NA |
| | Hexachloroethane | 40 | <MDL | 34-79 | NA |

## TABLE A7-3

## ANALYTICAL LABORATORY DATA QUALITY OBJECTIVES FOR PRECISION AND ACCURACY

| Parameter | QC Compounds | MS/MSD Precision (RPD) % | Blanks | LCS & MS/MSD Accuracy (%R) | Surrogate Accuracy (%R) |
|---|---|---|---|---|---|
| | Nitrobenzene | 40 | <MDL | 55-120 | NA |
| | Isophorone | 40 | <MDL | 61-114 | NA |
| | bis(2-chloroethoxy)methane | 40 | <MDL | 66-106 | NA |
| | 1,2,4-Trichlorobenzene | 40 | <MDL | 40-93 | NA |
| | Naphthalene | 40 | <MDL | 55-104 | NA |
| | Hexachlorobutadiene | 40 | <MDL | 23-83 | NA |
| | 2-Chloronaphthalene | 40 | <MDL | 48-112 | NA |
| | Dimethylphthalate | 40 | <MDL | 68-115 | NA |
| | Acenaphthylene | 40 | <MDL | 15-127 | NA |
| | 2,6-Dinitrotoluene | 40 | <MDL | 66-114 | NA |
| | Acenaphthene | 40 | <MDL | 57-116 | NA |
| | 2,4-Dinitrotoluene | 40 | <MDL | 66-111 | NA |
| | Diethylphthalate | 40 | <MDL | 66-123 | NA |
| | 4-Chlorophenyl-phenylether | 40 | <MDL | 52-128 | NA |
| | Fluorene | 40 | <MDL | 63-122 | NA |
| | 4-Bromophenyl-phenylether | 40 | <MDL | 59-120 | NA |
| | Hexachlorobenzene | 40 | <MDL | 59-123 | NA |
| | Phenanthrene | 40 | <MDL | 68-128 | NA |
| | Anthracene | 40 | <MDL | 65-125 | NA |
| | Di-n-butylphthalate | 40 | <MDL | 57-133 | NA |
| | Fluoranthene | 40 | <MDL | 66-121 | NA |
| | Pyrene | 40 | <MDL | 73-130 | NA |
| | Butylbenzylphthalate | 40 | <MDL | 72-121 | NA |
| | 3,3-Dichlorobenzidene | 40 | <MDL | 20-118 | NA |
| | Benzo(a)anthracene | 40 | <MDL | 57-137 | NA |
| | Chrysene | 40 | <MDL | 73-120 | NA |

**TABLE A7-3**

**ANALYTICAL LABORATORY DATA QUALITY OBJECTIVES FOR PRECISION AND ACCURACY**

| Parameter | QC Compounds | MS/MSD Precision (RPD) % | Blanks | LCS & MS/MSD Accuracy (%R) | Surrogate Accuracy (%R) |
|---|---|---|---|---|---|
| | bis(2-Ethylhexyl)phthalate | 40 | <MDL | 54-154 | NA |
| | Di-n-octylphthalate | 40 | <MDL | 65-127 | NA |
| | Benzo(b)fluoranthene | 40 | <MDL | 61-107 | NA |
| | Benzo(k)fluoranthene | 40 | <MDL | 74-128 | NA |
| | Benzo(a)pyrene | 40 | <MDL | 29-147 | NA |
| | Indeno(1,2,3-cd)pyrene | 40 | <MDL | 57-122 | NA |
| | Dibenz(a,h)anthracene | 40 | <MDL | 55-123 | NA |
| | Benzo(g,h,I)perylene | 40 | <MDL | 56-123 | NA |
| | 2-Fluorophenol | NA | NA | NA | 15-67 |
| | Phenol-d5 | NA | NA | NA | 4-53 |
| | Nitrobenzene-d5 | NA | NA | NA | 21-171 |
| | 2-Fluorobiphenyl | NA | NA | NA | 48-125 |
| | 2,4,6-Tribromophenol | NA | NA | NA | 40-136 |
| | Terphenyl-d14 | NA | NA | NA | 35-158 |
| Metals | Aluminum | 0-10 | <RL | 75-125 | NA |
| | Calcium | 0-10 | <RL | 75-125 | NA |
| | Magnesium | 0-10 | <RL | 75-125 | NA |
| | Potassium | 0-10 | <RL | 75-125 | NA |
| | Soldium | 0-10 | <RL | 75-125 | NA |
| | Antimony | 0-10 | <RL | 75-125 | NA |
| | Arsenic | 0-10 | <RL | 75-125 | NA |
| | Barium | 0-10 | <RL | 75-125 | NA |
| | Beryllium | 0-10 | <RL | 75-125 | NA |
| | Cadmium | 0-10 | <RL | 75-125 | NA |
| | Chromium | 0-10 | <RL | 75-125 | NA |

## TABLE A7-3

## ANALYTICAL LABORATORY DATA QUALITY OBJECTIVES FOR PRECISION AND ACCURACY

| Parameter | QC Compounds | MS/MSD Precision (RPD) % | Blanks | LCS & MS/MSD Accuracy (%R) | Surrogate Accuracy (%R) |
|---|---|---|---|---|---|
| | Cobalt | 0-10 | <RL | 75-125 | NA |
| | Copper | 0-10 | <RL | 75-125 | NA |
| | Lead | 0-10 | <RL | 75-125 | NA |
| | Iron | 0-10 | <RL | 75-125 | NA |
| | Manganeses | 0-10 | <RL | 75-125 | NA |
| | Mercury | 0-10 | <RL | 75-125 | NA |
| | Nickel | 0-10 | <RL | 75-125 | NA |
| | Selenuim | 0-10 | <RL | 75-125 | NA |
| | Silver | 0-10 | <RL | 75-125 | NA |
| | Thallium | 0-10 | <RL | 75-125 | NA |
| | Vanadium | 0-10 | <RL | 75-125 | NA |
| | Zinc | 0-10 | <RL | 75-125 | NA |
| Cyanide | | 10 | <RL | 70-123 | NA |
| Nitrate/Nitrite | | 10 | <RL | 69-121 | NA |
| Chloride | | 10 | <RL | 68-127 | NA |
| Sulfate | | 10 | <RL | 79-120 | NA |
| Carbonate/Bicarbonate | | 10 | <RL | NA | NA |
| Methane | | 40 | <RL | 59-131 | NA |
| Ethene | | 40 | <RL | 59-136 | NA |
| Ethane | | 40 | <RL | 60-138 | NA |
| Phosphate (Total) | | 10 | <RL | 75-125 | NA |
| TKN | | 12 | <RL | 71-145 | NA |
| Ammonium | | 12 | <RL | 60-126 | NA |

NA - Not available or not applicable

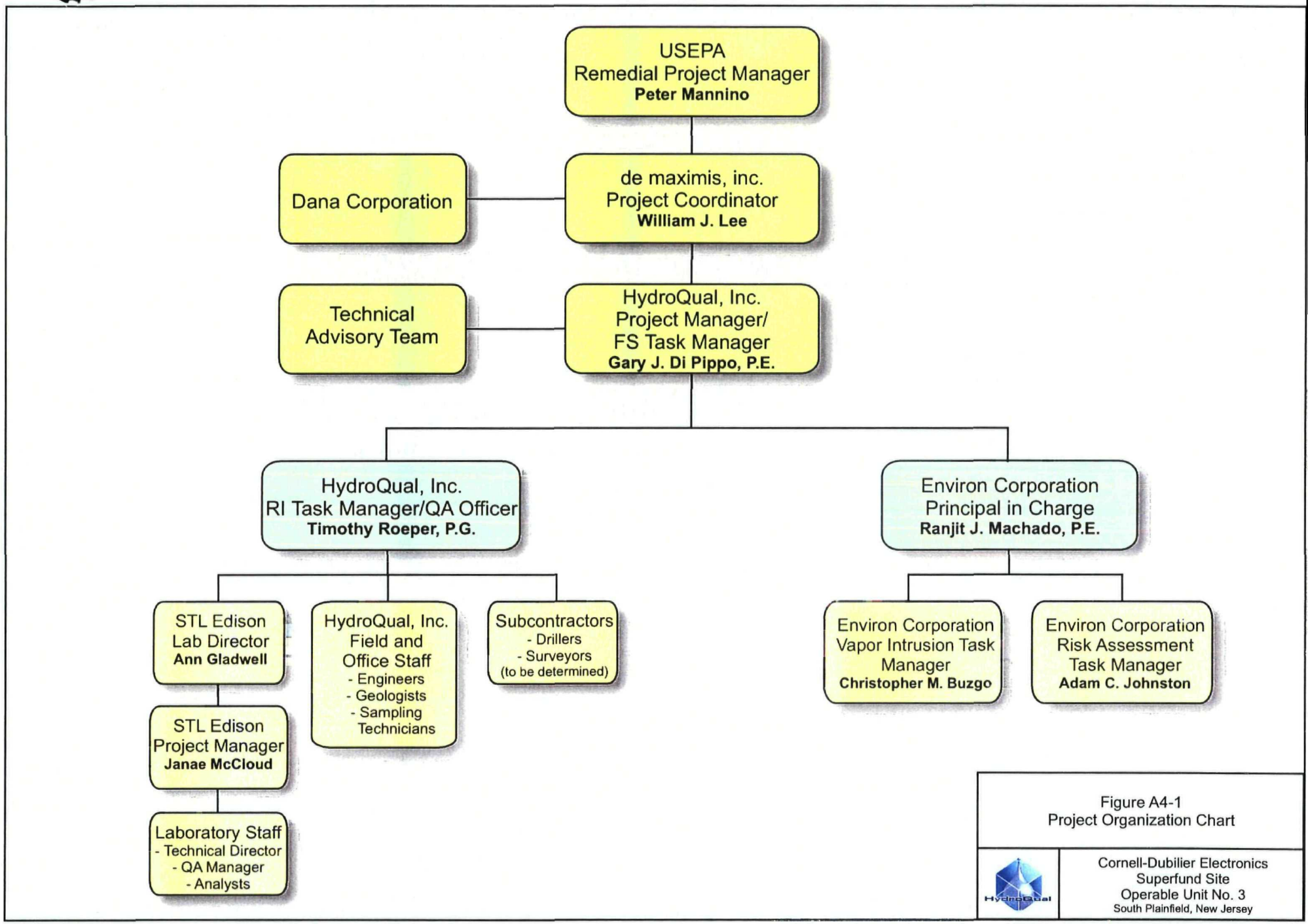



Figure A4-1
Project Organization Chart

Cornell-Dubilier Electronics
Superfund Site
Operable Unit No. 3
South Plainfield, New Jersey

# B MEASUREMENT/DATA ACQUISITION

## B1 Sampling Process Design (Experimental Design)

Initial sampling activities will focus on soil gas as a means to investigate the potential for vapor migration into indoor air and as a possible indicator of elevated VOC concentrations in the underlying groundwater. Stage 1 sampling areas (i.e., the initial sampling areas) have been identified based on review of historical groundwater data and earlier discussions with USEPA. Accordingly, soil gas samples will first be collected from areas along Hamilton Boulevard and Spicer Avenue, to the west and southwest of the site, respectively. In addition, soil gas sampling locations along New York Avenue will be included in the initial soil gas sampling activities to aid in finalizing the locations for proposed well locations D and E. Additional areas to be included in the initial phase of the soil gas sampling program include areas to the north of the site, south of Church Street. Preliminary soil gas sampling locations will be identified prior to commencement of field activities; however, the final locations will be determined based on access, building characteristics, to the extent practicable, and in response to the collected data. In this manner, the soil gas sampling program will proceed in an iterative manner, with decisions made based upon the observed conditions. Likewise, the need for soil gas surveys at additional areas (Stage 2 locations) will be dependent upon the results obtained from the Stage 1 locations.

Two samples are proposed to be collected from each of the locations identified on Figure 4-2 of the Work Plan, with samples collected from opposite ends of the building. The sampling locations are biased to include a greater number of properties in those areas proximate to the Site with fewer properties sampled in areas farther from the Site. To the extent possible, the soil gas samples will be collected from within approximately 10 feet of the building foundation (near-slab), which is recommended in the New Jersey Department of Environmental Protection Vapor Intrusion Guidance (NJDEP, 2005) to better define

potential impacts to indoor air when using exterior soil gas samples. If the samples cannot be collected from within 10 feet of the building footprint due to site conditions, access restrictions, etc., the samples will be collected as close to the building foundation as possible.

At least one sub-slab sample (or crawl space, if any), which will be representative of conditions directly underneath a building, will be collected from each of 15 locations identified on the basis of the soil gas survey. If the soil gas survey indicates no evidence of vapor intrusion, then the need for and/or extent of a verification sampling program using sub-slab/indoor air sampling will be developed in consultation with the USEPA, and if implemented would include up to 15 locations, selected on the basis of the collective data.

Crawlspace air/subslab air, unlike indoor air will not be affected by indoor sources (i.e., cleaners, solvents) and, therefore, should provide information on VOCs migrating from contaminated groundwater to the surface immediately beneath the residential buildings. While these crawlspace/subslab samples will not provide information on the actual amount of VOCs in the indoor air, they will provide information on the potential impact to indoor air from subsurface contamination. The sampling will be performed during two separate sampling events to account for seasonal variability. Each sample will be collected over a 24-hour period.

If the analyzed crawlspace/sub-slab samples exceed the screening criteria, indoor air samples will be collected within the living space of the building. The proposed location includes the basement, if the residential building has one, or if the building does not have a basement, in a commonly occupied part of the residential building, such as the living room, bedroom, or office.

Along with the collection of indoor air and crawlspace/subslab samples, one outdoor air sample per residential building will be collected. These samples will be used to assess the ambient outdoor air concentrations of VOCs that could impact indoor air. Outdoor samples will be collected over the same 24-hour period as the indoor air samples are

collected. In addition, co-located samples will be collected by placing two canisters side by side and opening the valves simultaneously.

The information obtained from the Stage 1 soil gas survey will also be used, as applicable, to provide adjustments to the locations selected for installation of groundwater monitoring wells. The current monitoring well locations have been selected based upon review of historical data and previous discussion/agreement with USEPA. Previous discussion with USEPA identified the wells as MW-A through MW-J, this nomenclature has been replaced with MW-100 through MW-109 and will be used from this point forward. The locations and basis for selection are summarized below and maps are provided in the Work Plan.

MW-100 (MW-A) – This location will be completed near existing well MW-06 and is intended to characterize the on-site vertical extent of groundwater impacts.

MW-101 (MW-B) – This location is located upgradient (southeast) of the site and is intended to characterize background water quality.

MW-102 (MW-C) – This location is also located upgradient but to the east-southeast of the site and is also intended to characterize background water quality.

Both of these locations (MW-101 and MW-102) will include a shallow bedrock monitoring well completed at the depth at which water is first encountered in the rock (approximately 30 – 50 feet below ground surface). A deep bedrock well will also be installed at one or both of these locations depending on the observed total volatile organic (TVO) concentration in the shallow bedrock interval at these locations.

MW-103 and MW-104 (MW-D and MW-E) – These two well locations are intended to provide additional water quality and water level information in the area previously investigated by NJDEP to characterize existing groundwater contamination in this area.

MW- 105 (MW-F) – This location has been selected for a shallow bedrock monitoring well (30 –50 feet below ground surface) to characterize groundwater quality immediately side gradient (west-southwest) of the site. The tentative location is located between domestic wells and on-site well MW-08 that have previously reported elevated TVO concentrations and domestic wells further to the west-southwest with lower reported TVO concentrations.

MW-106 (MW-G) – This location has been selected for a shallow bedrock monitoring well (30 –50 feet below ground surface) to characterize groundwater quality immediately side gradient of the site to the northeast. This well is intended to confirm the generally low TVO concentrations reported in on-site wells MW-02 and MW-03.

MW-107 (MW-H) – This location is intended to characterize groundwater impacts downgradient of the site and would include a shallow bedrock well in the upper 30 to 50 feet below ground surface and a deep bedrock monitoring well.

MW-108 (MW-I) – This location has been selected for a shallow bedrock monitoring well (30 –50 feet below ground surface) to further characterize groundwater quality downgradient from the site.

MW-109 (MW-J) - This location is intended to characterize groundwater impacts downgradient of the site and would include a shallow bedrock well in the upper 30 to 50 feet below ground surface, as well as a deep bedrock monitoring well.

Groundwater samples will be collected during the drilling process for field analysis to assist in determining when to set intermediate casings and the depth of investigation at each individual location; with a maximum depth established at 450 feet below ground surface (see Work Plan text for additional discussion). The field screening results will also provide a vertical profile of VOC concentrations with depth. The objective of the field analysis of groundwater samples is to provide semi-quantitative total VOC results for field decision-making.

Data collection efforts during the drilling program will also include the collection of rock core, (for matrix diffusion testing and stratigraphic correlation) downhole geophysical logging, including caliper, gamma, temperature, fluid resistivity, and as applicable, acoustical televiewer logs; and packer testing at ten foot intervals to measure hydraulic conductivity within the borehole (See SOP's in Appendix A). An aquifer test will be conducted to obtain information regarding the aquifer hydraulic parameters (transmissivity, storativity, anisotropy) and water level data will be collected to assess horizontal and vertical hydraulic gradients, groundwater flow direction and the interaction between surface water and groundwater. These data, coupled with water quality results obtained from laboratory analysis of groundwater samples collected from the new and existing monitoring wells, will be used to meet the SOW objective of "understanding the nature and extent of groundwater contamination at the site".

Given the presence of VOC constituents throughout the study area (See Work Plan for additional discussion), the sampling process design does not anticipate the installation of monitoring wells and the collection of groundwater quality data from locations at which non-detectable levels of VOCs are reported. Assuming this is the case, the sampling process has been designed to meet the objectives of the SOW through evaluation of concentration gradients, site specific constituents (when present), hydrogeologic characteristics of the underlying Passaic Formation (anisotropy, transmissivity, matrix porosity, diffusion coefficients, etc.), historic and current groundwater use, contaminant mobility, etc. The sampling process design, thus calls for the collection of various forms of data that will be integrated to meet the stated objectives.

The estimated number of samples collected from the various media discussed above is summarized on Table B1-1. The number of samples is estimated based upon the initial estimates of the scope of work. These estimates, however, are subject to change based upon the findings of the investigation as it proceeds.

# B2 Sampling Methods Requirements

## B2.1 Soil Gas Sampling

Prior to implementation of the field work, the owner of each of the properties selected for proposed sampling will be notified in writing at least one week in advance of the sampling and by telephone at least two days prior to the start of sampling. The property owner will be asked to sign an access agreement providing field personnel access to their property to perform soil gas sampling. An example access agreement is provided in Appendix B.

As discussed in the Work Plan, soil gas probes will be installed using direct push sampling techniques at approximately 114 locations proximate to the site. Soil gas samples will be collected from the vadose zone close to the water table, and at least 1 foot above the capillary fringe. The total depth of sampling will not exceed 20 feet below ground surface (bgs). To the extent possible, the samples will be collected from more than 5 feet bgs to minimize the potential for short-circuiting of ambient air. Each of the soil gas samples will be collected into Tedlar bags and analyzed using on-site mobile GC/MS laboratory equipment (Appendix B) for the following targeted chlorinated solvents:

- PCE
- TCE
- Cis-1,2-DCE
- 1,2,4-trichlorobenzene
- vinyl chloride

In addition to the approximately 114 soil gas samples analyzed using on-site mobile GC techniques, a subset of these (10% or 12 samples) will be collected into evacuated 1-L SUMMA canisters, and submitted to a New Jersey-certified fixed-base laboratory for analysis via USEPA Method TO-15 to verify the results of the on-site GC analysis and to identify a complete list of soil gas constituents. Additions to the list of VOCs subjected to on-site GC analysis may be made if constituents representing more significant risk levels than the selected VOCs are identified from the Method TO-15 analysis.

Two samples are proposed to be collected from each of the locations identified on Figure 4-2 of the Work Plan, with samples collected from opposite ends of the building. To the extent possible, the soil gas samples will be collected from within approximately 10 feet of the building foundation (near-slab), which is recommended in the New Jersey Department of Environmental Protection Vapor Intrusion Guidance (NJDEP, 2005) to better define potential impacts to indoor air when using exterior soil gas samples. If the samples cannot be collected from within 10 feet of the building footprint due to site conditions, access restrictions, etc., the samples will be collected as close to the building foundation as possible.

Soil gas samples will be collected in accordance with the U.S. EPA. *Environmental Response Team (ERT) Standard Operating Procedure (SOP) #2042 Soil Gas Sampling; June 1996* (See Appendix B) and the NJDEP October 2005 Vapor Intrusion Guidance.

## B2.2 Indoor Air sampling

Prior to implementation, the owner/occupant of the selected sampling location (residence) will be notified by telephone prior to the start of sampling and by an instruction letter through the mail. A copy of this letter, and the access agreement that the owner/occupant will be asked to sign allowing the field personnel to enter the building and to sample the indoor air, is provided in Appendix B

As noted in Section B1, initial indoor sampling will consist of the collection of sub-slab samples. Sub-slab samples will be collected in accordance with the draft USEPA document, *Standard Operating Procedure (SOP) for Installation of Sub-Slab Vapor Probes and Sampling Using EPA Method TO-15 to Support Vapor Intrusion Investigation* and *U.S. EPA ERT SOP #1704: Summa Canister Sampling* (Appendix B). In addition, sampling will be in accordance with the U.S. EPA Region II CERCLA Quality Assurance Manual; and U.S. EPA Superfund Program Representative Sampling Guidance OSWER Directive 9360.4-10, Interim Final, EPA/540/R-95/141, Office of Emergency and Remedial Response (OERR), Washington, DC.

In the case of crawl space sampling (performed if a slab is not present), in order to prevent outdoor air interference, crawlspace vents will be closed prior to and during sampling. Each vent will be covered with a high-density polyethylene barrier sheet. The sheet will be sealed on the outside of the vent with a tape adhesive. For buildings that contain sump pumps, a sample will be taken in or as close as possible to the sump pump. This sample will be used to determine if the sump pump is serving as a route of entry for contaminants into the indoor environment.

In the event that sub-slab samples exceed the screening criteria, indoor air samples will be collected from the basement or first floor living space by placing a SUMMA canister equipped with a regulator set by the laboratory to collect air over a 24-hour period. The sampler will open the canister to start the flow of air into the canister. While the canister is filling, the sampler will ask the resident questions from the Questionnaire (Appendix B) and survey the chemicals found in the residence. After 24-hours has elapsed the sampler will return to the residence, close the regulator, label the canister and prepare it for shipment to the laboratory.

The total possible number of samples for each building is 2 samples, in addition to laboratory quality control samples (i.e., field co-located sample) and an ambient air sample.

### B2.3 Groundwater Sample Collection

Groundwater samples will be collected during the drilling process for field screening analysis and from permanent monitoring points (monitoring wells). Each of these sampling processes is described below.

Groundwater samples collected during the drilling process for field screening analysis will be collected from isolated ten foot sections of the open rock borehole using a packer assembly as described in the Discrete Interval Packer Sampling SOP provided in Appendix A. The isolated interval will be purged to facilitate collection of a representative sample by pumping

approximately 10 volumes of the fixed 10 foot sampling interval. The pumping rate will then be lowered to 500 mL/min or less until the amount of water equal to the volume contained in the discharge tubing is evacuated. The groundwater sample will then be collected directly from the discharge tubing into the appropriate sample vial. Samples for field analysis will be collected in an un-preserved 40 ml VOA vial with headspace as called for in Color-Tec Field Screening SOP (Appendix A).

In the event that the selected interval yields less than one gallon per minute, and at the discretion of the site Hydrogeologist, the packers may be deflated and moved to an alternative depth within the borehole. The objective is to locate an interval that produces sufficient volume so that a representative sample can be collected. Intervals that yield low volumes of water have a greater probability of cross contamination from the open borehole prior to sealing off the selected interval. Purging activities should not exceed approximately 30 minutes per location.

Groundwater samples collected from typical two-inch diameter or larger monitoring wells will collected with a non-dedicated electric submersible pump (Grundfos Redi-Flo2) or bladder pump (Well Wizard) in accordance with the Low Flow/Purge sampling methodology as described in the Groundwater Sampling SOP in Appendix A. In the event that multi-port Water FLUTe wells are installed, groundwater samples will be collected directly from the dedicated sampling tubing in accordance with the manufacturers directions as detailed in FLUTe Liner System Installation and Operation SOP (Appendix A).

In the unlikely event that a sampling location is dry (contains less than 0.5 feet of water) a notation will be made on the field data sheet and a sample will not be collected from that location. Similarly, if a well is purged dry and does not recover within twenty four hours, the well will be considered dry for that sampling event and appropriately noted on the field data sheet. For wells, which recover only minimally, samples will be collected in the order described in the Groundwater Sampling SOP (Appendix A) until the available sample volume is expended.

Purge water generated during groundwater sampling activities will be containerized and transported back to the on-site staging area for proper handling.

## B2.4 Cleaning and Decontamination

Cleaning and decontamination of equipment used for drilling and sample collection will be conducted in accordance with Equipment Decontamination SOP (Appendix A). Submersible sampling equipment used for the collection of groundwater samples from two inch diameter or larger monitoring wells will be decontaminated prior to and between each use. Pump tubing will be discarded after each use. Cleaning and decontamination of the sampling equipment associated with the Water FLUTe installations (if installed) will not be required as the material is dedicated to each sampling point.

Cleaning and decontamination of the packer assembly, pump and related equipment used for collection of the field screening samples will be conducted between individual boreholes and after setting an intermediate casing within a borehole. Decontamination will not be required when collecting successive samples in an open borehole as the sampling equipment will be in contact with the borehole water. Purging of the isolated interval and the decision criteria associated with the field screening samples has been developed in recognition of these conditions.

Cleaning and decontamination of other equipment such as the drilling tools, geophysical instruments, etc., will be completed between each borehole location.

Cleaning and decontamination of the Color-Tec field screening equipment will not be required as new tubing, sample vials, calorimetric tubes, etc. will be used for each new sample. Likewise, Tedlar bags used for the soil gas sampling are for single use and do not required decontamination.

Summa canisters will be decontaminated by the laboratory prior to use and will be certified as clean. The Summa canisters will be cleaned according to:

- TO-15: *Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specialty-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air;* (See Appendix B) and

- *US. EPA Region II CERCLA Quality Assurance Manual.*

## B2.5 Inspection and Acceptance Requirements for Supplies and Containers

Upon receipt of the sampling containers, the field sampling team will inventory the sample bottles to verify that the required number and type of containers provided are consistent with the sampling requirements for the round of sampling. Discrepancies will be reported to the laboratory immediately and the laboratory will be responsible for providing the needed sample bottles within twenty four hours.

Supplies and/or containers associated with field analytical procedures will be inspected upon receipt for consistency with the required materials (e.g. the range of colorimetric tubes received will be confirmed with the order). The supplies will also be inspected for damage, discoloration, ineligible markings, etc. and replacements ordered as needed.

## B2.6 Identification and Correction of Sampling Problems

The Field Team Leader will be responsible for identifying sample collection problems. If the problem is relatively minor and would not have compromised the quality of the data, the Field Team Leader will correct the problem and document the occurrence. The QA Manager (Mr. Timothy Roeper) will be notified of identified sample collection problems and may require corrective measures over and above those proposed by the Field Team Leader. If the QA Manager determines that there is a risk of the problem resulting in compromised data, he will contact the Project Coordinator and USEPA's Project Manager to discuss the problem and potential corrective measures. If sample integrity/data are considered to be compromised, then a replacement sample will be collected while the field sampling program

is underway so that the replacement sample(s) may be directly integrated into the data set (i.e., no temporal variability issues).

# B3 Sample Handling and Custody Requirements

## B3.1 Requirements and Provisions for Sample Handling

Sample Containers and Preservatives

The specific requirements for container types, preservation methods, and maximum holding times for aqueous and air samples are listed in Table B3-1.

Sample Naming Conventions

Soil gas, sub-slab samples and indoor air sample ID's will be keyed to the sample locations and will indicate the type of sample collected and date of collection. Soil gas samples will be identified by the prefix "SG", Sub-slab samples by the prefix "SS" and indoor air samples with the prefix "IA". The nomenclature is as follows:

Soil Gas Samples
SG-SA01n-[date], where:
SG = soil gas sample; SA01n = Spicer Avenue ("SA") Survey Area sample location 01 collected from northern ("n") side of property; and the date of sample collection "yymmdd".
Sub Slab Samples
SS-SA01-[date], where:
SS = sub-slab sample; SA01 = Spicer Avenue Survey Area from the building at sample location 01; and date of sample collection "yymmdd"

Indoor Air Samples
IA-SA01-[date], where:
IA = indoor air sample SA01b = Spicer Avenue from building basement ("b") at sample

location 01; suffix ("f") will be used to indicate first floor if building is slab on grade; and date of sample collection "yymmdd"

Field screening samples collected from the individual boreholes will be identified with the prefix "FS" to identify it as a field screening sample followed by the borehole location ID and the depth interval from which the sample was collected. For example, a sample collected from location MW-100 at a depth of 110 to 120 feet would be designated as FS-100-110-120.

Samples collected from rock core for matrix diffusion testing would be designated similarly, however, a prefix of "RC" will be used to designate it as a rock core sample and the sample depth will likely be in tenths of feet. Using the example above, a rock core sample collected from the MW-100 location at a depth of 110.4 to 110.9 feet would be identified as RC-100-110.4-110.9.

Groundwater samples will be identified by the well location with a suffix of "S" or "D" added, as applicable, to identify the shallow or deep well at the specific location. In the event that multi-port Water FLUTes are installed, the sample ID will include the prefix "FL" to identify it as a Water FLUTe location followed by the location ID and the sample port numbered from the shallowest to the deepest in ascending order. For example, if location MW-100 consisted of a shallow bedrock well and a Water FLUTe installation with three sampling ports identified as 1 through 3 from shallowest to deepest, groundwater samples collected from these locations will be identified as MW-100S and FL-100-1, FL-100-2, and FL-100-3.

Rinsate blanks, trip blanks and duplicates will be identified by the prefix "RB", "TB", or "DUP", respectively, followed by the date of collection in the format of MM/DD/YY. For example, a duplicate sample collected on July 7, 2006 would be labeled as DUP-070706. In the event that more than one type of each of these samples are collected on the same day, and "A", "B", or "C" will be added to the end of the sample ID (i.e. DUP-070706A). The

location at which the duplicate is collected will be noted on the field data sheet for that location.

Sample Labels

Sample labels are required on sample containers for the primary purpose of sample identification. Specific field data need not be recorded on the labels as they would be recorded on field data sheets. The sample labels will contain the following information:

- Sample or location identification number
- Analysis to be performed
- Preservative (optional)
- Project name and number
- Date and time of sample collection
- Initials of sampler

Example sample labels are illustrated in Figure B3-1.

In the case of samples collected via disposable Tedlar bags, the bags will be labeled with appropriate identification number using a ballpoint pen or other non-permanent marker to avoid cross-contamination, and temporarily stored on ice in coolers prior to transferring to the mobile laboratory.

For the samples collected using SUMMA canisters, a canister tag, provided by the laboratory, will be securely affixed to each SUMMA canister and include only the canister identification number and the valve number and flow rate. The sample tags will be secured to the canister itself. Once sealed, samples will be placed back into the cardboard boxes that they were received in. Custody seals and strapping tape will then be affixed to the boxes.

Sample Shipment

Shipment of samples to an analytical laboratory is usually required upon completion of sample collection. Proper packaging is necessary in order to protect the sample containers, to maintain the samples at a temperature of 4°C, and to comply with applicable transportation regulations.

In general, samples are shipped using the laboratory courier service when possible. If needed, samples may be shipped via an overnight courier. The packaging normally includes a shippable insulated box such as an ice cooler and contains protective internal packaging materials such as foam sleeves. Some laboratories use proprietary sample packaging with integral internal packaging. In either case, provisions need to be made for maintaining the temperature of the samples with the use of re-freezable ice packs.

Regulations must be observed regarding the shipment of Dangerous Goods. Sample containers and certain field equipment may be defined as Dangerous Goods such that special requirements must be followed for their shipment. Air shipment of Dangerous Goods is regulated by the International Air Transport Association (IATA) as described in "Dangerous Goods Regulations" (IATA, 2001). IATA Regulations are updated annually. The U.S. Department of Transportation (DOT; 49 CFR) regulates shipment by ground. Furthermore, individual shippers (e.g., Federal Express) or other countries (international shipments) may have additional requirements for dangerous goods shipment.

Environmental samples, (e.g., groundwater, surface water, or soil samples) containing relatively low concentrations of contaminants, (regulated under 40 CFR) are currently exempt from Hazardous Goods regulations. 40 CFR 261.40(d) states, "A sample of solid waste or a sample of water, soil, or air which is collected for the sole purpose of testing to determine its characteristics or composition is not subject to this Part or Parts 262 through 267 or Part 124 of this chapter or to the notification requirements of Section 3010 of RCRA". Sample containers must be properly packed such that inadvertent spillage does not occur during shipment.

Environmental samples which are known to be or suspected to be toxic, corrosive, flammable, or those which emit a noxious or anesthetic annoyance or discomfort to passengers and/or flight crews when shipped by air, must be packed, labeled and shipped in accordance with current IATA regulations. Refer to "Dangerous Good Regulations" (2001), Section 3 - Classification.

Specific regulations exist (Shipment in Excepted Quantities) for the shipment of many reagents that are commonly used as preservatives and decontamination agents. Consequently, the shipment to the field site of "empty" sample containers containing small quantities of preservatives must be conducted in accordance with the regulations. The most significant limitations for the shipment of preservatives (IATA, 2001) involve those for nitric acid in which only small quantities (<0.5L) of low concentration (<20 percent) nitric acid can be shipped in a given sample shipment.

## B3.2 Chain-Of-Custody

Chain-of-custody procedures are designed to trace the sample from the time that it is collected until it, or its derived data, are used. Samples would be considered to be "in custody" under the following conditions:

- It is in personal possession.
- It is in personal view after being in personal possession.
- It was in personal possession when it was properly secured.
- It is in a designated secure area.

A chain-of-custody form (to be supplied by STL) is to be initiated at the time that the sample containers leave the site at which they are prepared, usually that of the analytical laboratory supplying the containers. Example chain-of-custody forms are included in Figure B3-2. It is important that the field personnel completely fill out the applicable sections of the form. The chain-of-custody forms will be placed in shipping containers, protected from

moisture using plastic bags (e.g., Ziploc®) and will accompany the containers during shipment to the laboratory. Chain of Custody seals will be placed on the outside of the cooler (shipping container). The field personnel collecting the samples will be responsible for the custody of the samples until transportation to the laboratory. Sample transfer requires the individuals relinquishing and receiving the samples to sign, date, and note the time of transfer on the chain-of-custody forms. The chain-of-custody is considered to be complete after it has been received and signed in by the analytical laboratory. A copy of the chain-of-custody record will be maintained by the field personnel along with the other field records.

Common carriers (i.e., Federal Express) are not expected to sign the chain-of-custody form. However, the bill of lading or airbill becomes part of the chain-of-custody record when a common carrier is used to transport the samples.

Samples are received at the laboratory by a designated Sample Custodian. The Sample Custodian removes the samples from the cooler and compares the sample labels with the information provided on the chain of custody form. If applicable, sample preservation, including temperature, is checked upon sample receipt (volatile water sample preservation is checked at the time of screening). When "compromised" samples are received, it is documented in the project folder and brought to the immediate attention of the Laboratory Project Manager. HydroQual is then contacted for instruction and if the decision is to proceed with the analysis, the project report will clearly indicate any of the above conditions and resolutions.

## B4 Analytical Method Requirements

The target parameters and corresponding analytical methodologies are summarized on Table B4-1. Standard operating procedures (SOPs) for the required analyses and associated laboratory procedures for groundwater samples are included in the Laboratory SOP's in Appendix A. Analysis and laboratory procedures related to soil gas and indoor air samples are provided in Appendix B.

# B5 Quality Control Requirements

## B5.1 Sampling Quality Control

Field quality control procedures are summarized in Table B5-1.

## B5.2 Laboratory Quality Control

Laboratory quality control procedures to be employed by STL are summarized on Table B5-2, and discussed below.

**Laboratory Data Validation and Quality Control Specifications**

Laboratory Data Validation

Analytical data generated by STL Edison undergoes a rigorous internal data validation procedure (external data validation is addressed in Section D). The process involves a number of checks, including sample validity, a peer review process, and verification of quality control values.

The data validation process begins in the laboratory. Prior to analysis, the analyst inspects the sample and available documentation to determine that it has been appropriately collected, handled, and stored. If any of these steps have been conducted improperly, the Laboratory Director or Client Services will be notified. The client will be notified of the problem by Client Services and a decision made by the client based on that conversation. The client will decide if the sample should be considered void or if analysis should be carried out and a qualifier/disclaimer made on the final report.

Analytical procedures are performed in conjunction with appropriate QC procedures, as defined in the STL Edison SOP manual. They ensure the reliability of their analytical data

by verifying that quality control tests are performed for each batch of samples and that the results of the QC tests fall within acceptable ranges. Hand written data is recorded with indelible ink and corrections are done with a single strike outline, the analyst's initials and date. After successful completion of applicable QC tests and the data is entered into the LIMS, the work is checked by another person trained in the analysis (peer review) and submitted to the QC Coordinator or designated alternate for review.

Secondary review is typically conducted by laboratory Section Supervisors or data review personnel. This review checks on QC data including tune checks, calibration checks, surrogates, blanks, matrix spikes, matrix spike duplicates, sample duplicates and analytes to make sure they are within calibration.

The Technical Manager, Laboratory Manager or Lab Director reviews the project for completeness. He/she checks the data and the Request for Lab Analysis (RFLA) form (i.e., address, client, contact, etc.) to ensure the requested samples and analyses have been completed, raw data and other records associated with the project and QC samples are included and the procedures in the QA program have been followed. The final report is checked against the data in the folder by the Laboratory Manager or his/her designee. The main paperwork is signed to indicate that the entire project has been reviewed. If there are no anomalies associated with the data, the report is signed and mailed. If there is a problem, the report is sent back to the appropriate section leader to correct. If corrections are not possible a non-conformance summary is completed explaining any situation that may need to be noted. This summary is completed and signed by the Laboratory Manager or senior chemistry personnel.

Software programs used in data validation, such as calculation work sheets, have undergone validation procedures including hand calculations to verify correct calculations.

Internal Quality Control

Internal QC measures are practiced regularly to verify the accuracy of STL's analytical results in each section of their laboratories.

The following is a summary of the quality control measures that are regularly practiced in each section to determine the accuracy of STL's methods, equipment, and analysts:

- Evaluation of the quality of glassware and reagents by analyzing glassware/reagent blanks
- Analysis of known compounds, such as commercial standards
- Duplication of samples (field and laboratory)
- Matrix blanks, duplicates and spikes
- Exchanges between analysts
- Regular calibration and maintenance of instruments and equipment

STL Performance Evaluation results are stored in the QC office. Control charts of QC results are available for review when needed.

STL requires their subcontract laboratories to adhere to approved quality control plans, and to be accredited by appropriate national organizations such as NVLAP, AIHA, and New Jersey Department of Environmental Protection. Subcontract labs must perform all required QC procedures associated with the methodologies prior to analysis of STL samples. They are subjected to audits and/or site visits to ensure quality is kept.

This Quality Assurance program is reviewed on an annual basis. Review is the responsibility of the QA Coordinator. The review process will include section

leaders from all laboratory sections. Revisions to the QA manual will be made and approved by the QA Coordinator and Laboratory Director.

Accuracy and Precision

Analyses are monitored daily for precision and accuracy. Specific checks are prepared for individual analyses. Their definitions are as follows:

- Sample Batch: A group of samples that are similar with respect to the sampling and testing procedures. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will be handled as a separate batch. Any time a new standard is prepared or a fresh reagent introduced into the analytical procedure, a new batch is required.

- Calibration: A response curve where specific units, (i.e., peak height, peak area, or absorbance units) are mathematically correlated to the concentration of the analyte introduced into the instrument. A multiple point curve (usually 5) is constructed so as to bracket the expected sample concentration. The linearity of the calibration curves should be > 0.995. A new calibration curve is constructed on a daily basis for I.H. work depending on the analytes requested.

- Blanks: Artificial sample designed to monitor the possibility of the introduction of contaminants.

  1. Glassware and Reagent/Method Blanks contain all reagents involved in the analysis and are prepared and analyzed as a sample - at least 5% or one per batch. For a blank of this type to be acceptable, the concentration of any analyte of interest in the blank should not be higher than the highest of either:

     - the method detection limit,
     - five percent of the regulatory limit for that analyte, or

- five percent of the measured concentration in the sample.

2. Field/Equipment Blank: taken to the field and opened to show the effects of the container being exposed to the environment then prepared and analyzed as a sample. Alternatively, the contents of the bottle are poured over decontaminated equipment and the contents are collected and analyzed to evaluate the effectiveness of the decontamination efforts.

3. Media Blanks: contains all reagents involved in the analysis as well as any media used in sampling and prepared and analyzed as a sample- at least 5% or one per batch.

   - Post Digestion Spikes: A known amount of analyte is added to a sample and analyzed to determine percent recovery. Spikes are analyzed at a frequency dictated by specific methods.

   - Blank Spikes: A known amount of analyte is added to analyte-free water and prepared and analyzed as a sample. One will be run with each batch of samples.

   - Matrix Spikes: A known amount of analytes of interest are added to a specific sample that is then prepared and analyzed as a sample.

   - Matrix Spike Duplicates: A known amount of analytes of interest are added to the same sample as the matrix spike and then prepared and analyzed as a sample.

   - Surrogates: Compounds that behave similarly to those being analyzed but are not normally found in the environment are used as surrogates to monitor analyses. Known amounts of these compounds are added to each sample prior to analysis.

- Quality Control Checks: Standards prepared from a source other than that which was used to calibrate the instrument. They are used to verify calibration and procedural accuracy.

- Initial Calibration Verification (ICV): Check standard made from a different stock solution than the calibration standards to check the calibration curve. It is to be run at the beginning of the analytical run.

- Continuing Calibration Verification: Same as ICV, but run after every 10 - 20 samples depending on the method, in an analytical run.

Statistical Determination of Precision and Accuracy

Accuracy is a statistical measurement of correctness and includes components of random error (variability due to imprecision) and systemic error. It therefore reflects the total error associated with the measurement. Analytical accuracy is measured by comparing the percent recovery of analytes spiked into a Laboratory Control Sample (LCS) also known as a blank spike. For some organic compounds surrogate recoveries can also be used to assess accuracy and method performance for each sample analyzed.

Accuracy of matrix spike recoveries is used to evaluate matrix effect in individual samples for a specific site. Matrix spike data is not used as the primary accuracy determination for laboratory QC purposes. Specific methods do have very wide "recommended" limits for controlling laboratory data.

The percent recovery of each matrix spike is calculated by:

$$\frac{SS - S}{SA} X\ 100 = \text{Percent Recovery}$$

Where: SS = spike concentration + sample concentration

S = sample concentration

SA = spike

When at least 30 samples have been analyzed, the mean recovery and the standard deviation from the mean recovery are calculated and plotted in a control chart using the following calculation.

$$\%R_m = \frac{3\%R_i \cdots \%R_n}{n}$$

$$S = \frac{3_i^n (\%R_i - \%R_m)^2}{n-1}$$

Where: %Ri = %Recovery of each data point

%Rm = %Recovery of the mean of the data points

n = number of data points

S = Standard deviation

The control limits of the data have been set at $\pm$ 3 standard deviations from the mean recovery. Warning limits have been set at $\pm$ 2 standard deviations from the mean. Control charts are printed and reviewed for trends quarterly by the QA/QC Coordinator.

Precision is evaluated by analysis of duplicate sample results.

$$RPD = \frac{\breve{s}O - D\breve{s}}{(O+D)/2} X\,100$$

Where: O = Original sample

D = Duplicate sample

When at least 30 samples have been analyzed, the mean RPD and the standard deviation from the mean are calculated and plotted in a control chart using the following calculation. Control charts are printed and reviewed for trends quarterly by the QA/QC Coordinator.

$$M = \frac{3m_i \cdots m_n}{n}$$

$$S_m = \frac{3_i^n (m-M)^2}{n-1}$$

Where: m = RPD of a replicate pair
M = mean of the RPD determinations
$S_m$ = Standard deviation of the data set RPD determinations
n = number of determinations

Control limits are 80 – 120 % RPD or as specified by the methods. In cases where no such limit has been set, laboratory limits of $\pm$ 3 standard deviations from the mean RPD are used.

The method detection limit is the laboratory established smallest amount of analyte that can be measured and reported with 99% confidence that the concentration is greater than zero. A set of seven standards are prepared at a concentration 1 - 10 times the estimated detection limit. The seven standards are analyzed as if they were samples.

The standard deviation of the measurements is calculated using the following calculation:

$$M = \frac{3m_i \cdots m_n}{n}$$

$$S = \frac{3_i^n (m-M)^2}{n-1}$$

Where: m = individual measurements

M = mean of the measurements

n = number of measurements

S = standard deviation of the measurements

The method detection limit is determined by multiplying the standard deviation of the measurements by the student's "t" value for a 99% confidence level and a standard deviation with "n – 1" degrees of freedom. When n = 7, the "t" value at a 99% confidence level is 3.14.

The method detection limits are updated annually.

The estimated quantitation limit is the lowest concentration of analyte that can be achieved with some degree of reliability under normal operating conditions. The practical quantitation limit may vary depending on the sample, but generally it is 5 - 10 times the method detection limit. See Table A7-1 for Method Detection Limits.

### B5.3 Field Analysis Quality Control

Quality control for field analytical procedures will be conducted by following the established SOPs so that that preparation, analysis, and reporting of the results is performed consistently. This includes heating of the groundwater sample vials and colorimetric tubes to consistent temperatures, observing purge times to identify failure of the purge pump, consistent completion of the field data sheet, etc. In addition, a representative number of field screening samples will be split for laboratory analysis for comparison of laboratory-derived results to the field screening methods.

Calorimetric tubes used in the field analysis will be inspected before use and discarded if broken, discolored or unreadable.

## B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Equipment (field and laboratory) is maintained, inspected, and cleaned according to the manufacturer's specifications. Any defective equipment is taken out of service until it has been shown to perform satisfactorily.

The following field instruments may be used during site characterization activities:

- Photoionization detector (PID) – Thermo OVM or equivalent
- Organic vapor analyzer (OVA) (optional) -FoxBoro Model 108 or equivalent
- Turbidity meter – Heriba-U22 or equivalent
- pH meter– Heriba-U22 or equivalent
- Specific conductivity meter – Heriba-U22 or equivalent
- Thermometer – Heriba-U22 or equivalent
- Dissolved Oxygen Meter – Heriba-U22 or equivalent
- Electronic water level meter – Solinist or equivalent
- Downhole, geophysical logging unit – Mount Sopris – MGX-II

Monitoring equipment will be protected (as much as practical) from contamination during field exploration without hindering operation of the unit. Operation of the equipment will be in accordance with the manufacturer's instructions provided with each piece of equipment.

The laboratories employ a system of preventive maintenance in order to prevent system down time, minimize corrective maintenance costs and ensure data validity. General preventive maintenance procedures, many of which are unique to particular instruments, are outlined in each instrument's operation manual. Routine maintenance is performed as recommended by the manufacturer. The manuals also assist in the identification of commonly needed replacement parts, so that an inventory of these parts can be maintained

at the laboratory. It is the Section Supervisor's responsibility to make sure that the most current version of the operator manual is available in the laboratory. Routine maintenance is performed by the analyst while external technicians may be called in for major repairs. In addition, an in-house instrument specialist who has received training for repair of all major pieces of laboratory equipment is available.

A bound maintenance and repair log notebook is kept with each instrument to record routine and non-routine maintenance. Notation of the date and maintenance activity is recorded every time service procedures are performed. This includes routine service checks by laboratory personnel as well as factory service calls. If problems occur, equipment is not used for routine analysis until a trained service representative for that instrument services the equipment and/or the instrument has been shown to operate properly (i.e., by retention time verification, response factor verification etc.). The return to analytical control following instrument repair is also noted in laboratory maintenance logbooks.

In addition to the above, the testing, inspection, and maintenance procedures for laboratory equipment include those summarized below:

- Annual measurements of hood velocities are performed. The measurements are posted near the hoods and copies filed by the Chemical Safety Officer.

- The analytical balances are calibrated annually by service personnel. Two class S weights within the range of normal use are used to check the calibration daily. These are recorded in bound logbooks stored near each balance. The class S weights will be recertified every 2 years.

- The refrigerators are maintained at 4° ± 2°C and the freezers at <0°C. Each are equipped with thermometers. These temperatures are checked daily and recorded in bound logbooks. Should the temperatures be outside the acceptance range, (4°C + 2°C for refrigerators and –10°C - -20°C for freezers) the facilities and maintenance manager should be notified to make adjustments. If the temperatures

are outside the acceptance range for a second consecutive day, the samples should be moved and professional service be requested.

- Temperatures of drying ovens and incubators are monitored daily and recorded in bound logbooks stored in plastic folders near the equipment. If the temperature falls outside the acceptance limits (as per method), the facilities maintenance manager should be alerted. If the temperature falls outside the acceptance limits after adjustment by the facilities maintenance manager, professional service should be requested.

- Thermometer calibration will be checked annually against a NIST thermometer by ASTM method E77-98 and the results recorded and stored in the Lab Manager's office.

Equipment and reference material records include the following:

- Name of item
- Manufacturer, identification, serial number
- Copy of manufacturer's instructions or manuals
- Details of maintenance carried out to date
- History of damage, malfunctions, modification, or repair

Service of equipment is performed by quality service organizations. Records and certificates from service calls are retained.

General laboratory support equipment is calibrated/verified annually using National Institute of Standards and Technology (NIST) traceable references over the range of use. Balances, ovens, refrigerators, freezers, incubators, and water baths are checked with NIST traceable references (where possible) and recorded. Additional monitoring as prescribed by the test

method SOP is recorded. Mechanical volumetric dispensing devices are checked for accuracy quarterly and recorded.

## B7 Instrument Calibration and Frequency

Instrument calibration procedures for field instruments will be performed in accordance with the manufacturers guidelines for the specific instrument used. Calibration of the equipment will be conducted each day in accordance with the manufacturer's instructions. If calibration is not maintained, the equipment will be placed on hold and not used until calibration is confirmed. Information related to calibration will be recorded in the field logbook and will include the instrument ID, date and time of calibration, calibration standard, and record of calibration measurement.

STL's procedures relative to instrument calibration and frequency are summarized below:

- Instruments must be calibrated prior to use to ascertain that they are operating properly within a particular range.

- Instruments are calibrated with standard solutions purchased from reputable suppliers. A great deal of care is taken to ensure that the standards are not contaminated with any other substances, and that they are not used beyond the expiration date.

- The frequency of calibration and the concentration of calibration standards are determined by the analytical method.

# B8 Inspection/Acceptance Requirements for Supplies and Consumables

The inspection/acceptance requirements for supplies and consumables are summarized on Table B8-1 and discussed below:

Preparation and Storage of Standards, Reagents and Samples

- Standards, reagents and samples are prepared in accordance with applicable safety regulations and recommendations, as deemed necessary by the Chemical Hygiene Officer. Hazardous reagents are prepared and used under a fume hood, and personnel are required to wear appropriate protective clothing such as safety glasses, gloves, and laboratory coats.

- Hazardous standards and reagents must have legible labels and the analysts are required to know the nature of the hazard, necessary safety measures, and emergency procedures.
- Stock standards are stored according to method requirements; Room temperature, 4°C ± 2°C or -10 – -20°C depending on the nature of the standard. Standards and samples are stored in separate refrigerators.

- Standards and samples are stored and used in areas with appropriate ventilation, well separated from compounds that might react or cross-contaminate.

- New standards are tested for quality and potential contamination by comparison of response factors.

- Stock standards are used for a maximum of one year after the date the standard is opened. Gas standards are ordered on an as needed basis. Standards and reagents are purchased at the quality/purity specified in individual methodologies.

- Carrier gases are purchased at the purity specified in the individual methodologies.

- Working standards and reagents are prepared as frequently as required by specific methods.

- Standards, samples and reagents are brought to room temperature prior to use, when necessary, in accordance with the individual SOPs.

- Regular inventories are taken to ensure proper supplies of reagents, and to verify that reagents are not past expiration dates. No reagent or standard is used past its expiration date. Expiration dates are to be written on the label. Outdated reagents and standards are disposed in accordance with STL Edison waste disposal program. Stock standards are not recertified.

- Reagent/Standard Preparation Logs are maintained for reagents that contain a mixture of chemicals. Amounts of chemicals used, date the reagent was made, and lot number of stock reagents, are recorded and initialed. Purchased standards must be traceable to NIST standards. Certificates of Analysis are kept on file in the individual sections.

- Purchased reagents are inspected and initialed upon receipt for visible defects. Purchased reagents are labeled with the date on which they were first opened. If the manufacturer does not provide an expiration date, then one will be assigned. Generally, commercial solutions are stored for two years after receipt or one year after opening with the exception of pH buffers that are replaced at least every six months. Dry reagents are used for six years after they are received. All chemicals are replaced more frequently if the substance has a physical change (i.e., color, physical state, and crystallization).

- Directions for the preparation of reagents are found as part of each method, any changes will be noted in the SOP Manual.

- Prepared solutions must be labeled with a properly filled out NFPA Diamond showing its hazardous characteristics plus the initials of the analyst who prepared the solution, the date of preparation, purity, concentration of the solution, and expiration date.

- Reagents are tested for quality and potential contamination by standardization techniques and using glassware/reagent blanks during analysis. See methodologies for specific reagent requirements. If not stated, ACS grade reagents or better are purchased.

- Titrants are standardized prior to each use or as indicated by the standard operating procedure.

- Volatile reagents are stored in the flammables cabinets or explosion proof refrigerators and used in areas with appropriate ventilation.

- When applicable, samples and standards are stored at $4° \pm 2°C$.

- Samples must be appropriately labeled and accompanied by a chain-of-custody.

- After analysis, QC checks, and data reviews have been completed, samples are retained for 30 days prior to the appropriate disposal or returned to client (if requested by the client in writing prior to analysis).

- Hazardous substances must be appropriately labeled prior to disposal or shipment to client. Detailed information regarding disposal of hazardous samples is provided in the Waste SOP.

# B9 Data Acquisition Requirements (Non-Direct Measurements)

In addition to the collection of regional data through the installation of monitoring wells (direct measurement), regional water quality information will be obtained through NJDEP well record searches, and other publicly available documents related to the surrounding area. One aspect of these data acquisition efforts relates to the public and residential well search discussed in the Work Plan, from which an understanding of regional groundwater use through time will be evaluated. An understanding of regional water quality and groundwater use will provide information to assess historical groundwater flow patterns and contaminant distribution.

# B10 Data Management

## B10.1 Field Record Keeping

Field records that are both technically and legally defensible must be maintained for the various aspects of groundwater and sediment sampling. These records include technical field data, sample identification labels, and chain-of-custody information for each sample. These records are described in the following sections.

Every attempt will be made to organize the sampling records prior to the commencement of field sampling activities. This will include the inventory and labeling of sample containers and the initiation of field data records and chain-of-custody forms. Technical field records are described below. Sample labels and chain-of-custody records have been described previously.

Field records must be maintained regarding the various aspects of groundwater sampling activities. The field records for groundwater sampling shall be made on preprinted, Groundwater Sampling Field Data Sheets. The use of a preprinted form is preferred due to the prompting that is provided for each aspect of record keeping, the ease of use, and the

consistent format that is provided. An example of the groundwater sampling data sheet and Groundwater field analysis data sheet is found on Figures B10-1 and B10-2.

The field sampling records (Sample Data Sheet) will include the following information:

- Sampling location
- Date and time
- Sampling personnel
- Condition of the well
- Static water level (depth to water)
- Depth to the bottom of the well
- Calculated well volume
- Purging method
- Actual purged volume
- Sample collection method
- Sample description
- Field meter calibration data
- General comments (weather conditions, etc.)

For the soil gas survey and subsequent indoor air sampling, all the relevant Containers (Tedlar bag or Summa canister) Sample Data Sheets, Questionnaires, and the field notebook will be completed for each sample collected. The Canister Sample Data Sheet (Appendix B) will be provided by the laboratory and records the sample location, sampling period, initial and final sample time and comments. As previously discussed, in case of the indoor air sampling, the Questionnaire (Appendix B) will establish an inventory of products such as cleaners, solvents, etc, that were present in the residential building at the time of sampling. In addition, the Questionnaire will record sample location; residential information; time of sample drop off and pick up; conditions in the room; laboratory sample number; laboratory sample analysis and sample collection notes and/or observations.

Data entries will be made using black indelible ink and will be written legibly. Entry errors

will be crossed out with a single line, dated, and initialed by the person making the correction. The field team leader will be responsible for reviewing the field notes and resolving transcription errors on a day-by-day basis. The QA Manager (Mr. Timothy Roeper of HydroQual, Inc.) will also review the field sampling records for accuracy and consistency.

In addition to the data sheets described above, a field notebook will be used by field personnel to record various aspects of sample collection and handling, visual observations, chronology of events, weather conditions, visiting personnel, field measurements, etc. The field notebook is a descriptive notebook detailing site activities and observations so that an accurate, factual account of field procedures may be reconstructed. This field notebook will be a bound weatherproof logbook that shall be filled out as the work proceeds.

## B10.2 Laboratory Data Tracking and Reporting

The laboratories utilize custom designed Laboratory Information Management System (LIMS) to uniquely identify and track samples (upon receipt at the lab as described in Section B3.2) and analytical data throughout their facilities. This information is stored as part of the Job data which is identified by a unique Job Number. Each sample is assigned a unique laboratory ID number. Two labels with this number are placed on each container of the sample (one on the side and one on the top). If there is more than one container per sample a letter suffix is assigned to track each container. Once labeled, the samples are placed in the appropriate storage area.

Once the Job Number has been generated, method specific analytical worksheets are generated for distribution to the appropriate supervisors and analysts. A secondary review of the Job Number is carried out by the Laboratory Project Manager to ensure compliance with project requirements. When the laboratory is ready to analyze a sample, an analyst requests the appropriate sample aliquot from the Sample Custodian by presenting their sample request worksheet. The analyst may be required to sign an internal chain-of-custody form when removing the sample aliquot from the sample management area based on the project requirement.

Analytical data will be reported consistent with the NJ Full Data Package requirements as well as in electronic format. The turn-around time for the electronic data deliverable and hard copy from the laboratory's receipt of the last sample of the sample delivery group will be 30 business days. The contents of the data deliverables are outlined below, followed by a description of the format and content of the electronic deliverable.

The Full Data Package will include the following contents (as applicable).

- Results Summary
- Chain-of-Custody
- Laboratory Chronicles
- Method Review
- Data Reporting Qualifiers
- Non-Conformance Summary
- Chromatograms where applicable
- Tuning, Method Blank, Calibration, Surrogate, Spike Recovery and Internal Standard area summary where applicable
- Injection logs for all samples and QC
- Extraction logs
- ICP Interference Check and Serial Dilution summaries for Metals
- Metals prep logs
- Metals Raw data
- Analysis runs logs for Metals
- QC results summary for General Chemistry
- General chemistry raw data

Electronic Deliverable

Analytical data will be available in either Excel or Access electronic formats. The fields to be included in the electronic deliverable will include the following:

- Field Sample ID
- Laboratory ID
- Date of Sample
- Date of Extraction
- Date of Analysis
- Analytical Parameter
- Analytical Result
- Methodology
- Method Detection Limit
- Sample Detection Limit
- Data Qualifiers
- CAS Number (where applicable)

## B10.3 Data Reduction, Storage, and Retrieval

Water level data will be manually transferred from the field data sheets and/or log book into a Microsoft Access Database established specifically for the Cornell-Dubilier Electronics monitoring program. Reduction of the data to groundwater elevations will be completed within the database by subtracting the depth to water from the surveyed reference elevation. A separate database file will also be maintained for the analytical data. The laboratory will provide the data in electronic format as described above and the data will be directly imported into the database. QA/QC checks will be run within the database to verify that sample and parameter names are consistently and correctly used, and a unique laboratory ID number identifies each sample. The duplicate samples will be identified from the sampling data and recorded in the database. The original laboratory diskette will be write protected

and maintained in the file. The database will be maintained on a network server and will be routinely backed-up.

The database will be maintained and updated following each sampling event and will serve as the primary means of data storage and retrieval. Queries will be written within the database as needed to tabulate and/or evaluate the data as needed.

HydroQual, Inc. will maintain the hard copy project files in a secured, limited access area for ten years after issuance of a ROD or commencement of construction of the remedy as selected in the ROD, whichever is later. The project files will contain, as applicable, relevant reports, records, correspondence, field logbooks, logs, original laboratory data packages, pictures, chain-of-custody records/forms, and subcontractor's reports. Copies of any pertinent records will be provided to the Agencies as needed. Electronic files will be maintained for a minimum of ten years as noted above.

TABLE B1-1

SUMMARY OF SAMPLES FOR COLLECTION AS PART OF THE OU-3 RI/FS WORK PLAN

| Sample Type | Estimated Number of Samples[1] | Matrix | Field/Lab analysis | Parameters |
|---|---|---|---|---|
| Soil Gas | 114 | Air | Field | Targeted chlorinated volatile organic compounds (CVOCs) |
| Soil Gas | 12 | Air | Lab | TO-15 Volatile Organics |
| Indoor Air (includes sub-slab)[2] | 15 | Air | Lab | TO-15 Volatile Organics |
| Discrete Interval GW Samples | 21 | Water | Field | Total Chlorinated Volatile Organics |
| Discrete Interval GW Samples | 5 | Water | Lab | TCL Volatile Organics |
| Monitoring Well Samples | 26 | Water | Lab | TCL VOCs, SVOC, Pest/PCB's, TAL Metals |

1- The actual number of samples will be dependant upon the results of the investigation.

2 - Number represents the first round of sub-slab samples. Additional samples will be collected if the sub-slab results are above the applicable screening criteria.

**TABLE B3-1**

**REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES**

| Analytical Parameter | Typical[b] Volume Required (mL) | Container[a] | Preservative | Maximum Holding Time |
|---|---|---|---|---|
| Volatile organic compounds (Water) (VOCs) | (3) 40 mlVials | G/vial Teflon®-lined septum | Cool, 4°C & HCl to pH<2[c] | 14 days[c] |
| Volatile organic compounds (Air) | 1L/6L[D] | Summa Canister | - | 30 days |
| Chlorinated volatile organic compounds (Air) | 1L | Tedlar Bag | - | 24 hours |
| Semi volatile organic compounds (SVOCs) | 1000 | AG/vial Teflon®-lined cap | Cool, 4°C | 7 days/extraction +40 days/analysis |
| TAL Metals | 1000 | P | $HNO_3$ to pH<2 | 6 months |
| Cyanide | 500 | P | Cool, 4°C NAOH to pH >12 | |
| Miscellaneous | | | | |
| Chloride | 100 | P | Cool | 28 days |
| Nitrate/Nitrite | 50 | P | Cool, 4°C & $H_2SO_4$ to pH<2 | 28 days |
| Sulfate | 100 | P | Cool | 28 days |
| Carbonate/Bicarbonate | 200 | P | Cool | 14 days |
| Methane ,Ethane,Ethene | (2) 40 ml Vials | G/vial Teflon®-lined septum | Cool, 4°C & HCl to pH<2[c] | 14 days[c] |

## TABLE B3-1 (CONTINUED)

## REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

| Analytical Parameter | Typical[b] Volume Required (mL) | Container[a] | Preservative | Maximum Holding Time |
|---|---|---|---|---|
| Volatile Fatty Acids | | G/vial Teflon®-lined septum | | |
| Phosphate | 100 | P | Cool, 4°C & $H_2SO_4$ to pH<2 | 28 days |
| TKN | 500 | P | Cool, 4°C & $H_2SO_4$ to pH<2 | 28 days |
| Ammonium | 500 | P | Cool, 4°C & $H_2SO_4$ to pH<2 | 28 days |

NOTES:

a. Polyethylene (P) or Glass (G) or Amber Glass (AG).
b. Analytical laboratory should be consulted for specific volume requirements.
c. Samples receiving no pH adjustment must be analyzed within 7 days.
d. 1L canister for soil gas – 6L canister for indoor air

## TABLE B4-1

## ANALYTICAL PARAMETERS AND METHODS FOR OU-3

| Analytical Parameters | Laboratory |
|---|---|
| TCL Volatile Organic Compounds (VOCs)* | EPA624 |
| Chlorinated VOCs in Soil Gas (Field) | 8021 |
| Volatile Organics in Air (Laboratory) | TO-15 |
| TCL Semi Volatile Organic Compounds* | EPA625 |
| TAL Metals* | 6010B/7470 |
| Nitrate/Nitrite | EPA 353.2 |
| Chloride | SM4500-Cl B |
| Manganese (Total) | SEE METALS |
| Iron (Total) | SEE METALS |
| Sulfate | EPA375.4 |
| Carbonate/Bicarbonate | SM2320B |
| Methane | 3810 Modified |
| Ethene/Ethane | 3810 Modified |
| Volatile Fatty Acids | Dionex proprietary method[1] |
| Phosphate (Total) | EPA365.2 |
| TKN | EPA351.2 |
| Ammonium | EPA350.2+350.1 |
| PCBs | 8082 |

Notes:

* See Table B1-1 for specific list of compounds.

[1] This method is a modification to Standard Method 5560 Organic and Volatile Acids (See SOP Appendix A)

**TABLE B5-1**

**FIELD SAMPLING QUALITY CONTROL**

| Field QC | Minimum Frequency | Control Limit/ Measurement Performance Criteria | Corrective Action (CA) | Persons Responsible For CA | Data Quality Indicator |
|---|---|---|---|---|---|
| Rinsate blank (water) | 1 per 20 samples | All compounds of interest ≤ RL | Qualify Data | Project Manager | Evaluate sample handling and collection procedures. |
| Trip blanks (VOC only) (water) | 1 per sample shipment or 1 every other day, whichever is greater | All compounds of interest ≤ RL | Qualify Data | Project Manager | Evaluate cross contamination of samples during shipment. |
| Cooler temperature blanks (water) | 1 per cooler | 4 ± 2 °C | Qualify Data | Project Manager | Evaluate representativeness and bias |
| Field duplicate (water and air) | 1 per 20 samples | ± 20% RPD with provisions for wider acceptance limits near the detection limits[1] | Qualify Data. | Project Manager | Evaluate precision and representativeness taking into account sample matrix variability |
| Lab/Field Comparison (air) | 1 per 10 samples | ± 20% RPD with provisions for wider acceptance limits near the detection limits[1] | Qualify Data. | Project Manager | Evaluate precision and accuracy of field measurements as compared to lab results |
| Lab/Field Comparison (water) | 1 per 10 samples | NA | Establish correlation | Project Manager | Establish correlation between field screening results and lab results for total chlorinated VOCs. |

Notes:

1 In accordance with USEPA Functional Guidelines for evaluating CLP data.

TABLE B5-2

LABORATORY QUALITY CONTROL

| Type | Frequency | Measurement Performance Criteria | Corrective Action (CA) | Person Responsible For CA | Data Quality Indicator |
|---|---|---|---|---|---|
| Method blank | Minimum of 1 per analytical batch or per 20 field samples; whichever is less. | All compounds of interest below RL. | Reanalyze. If second blank exceeds criteria, Clean and recalibrate. Document CA. | Laboratory Analyst | Evaluate cleanliness of sample preparation and analysis procedures. |
| Instrument blank | As needed due to instrument malfunction. | As specified by the manufacturer. | Locate source of problem and correct. | Laboratory Analyst | Evaluate the stability and accuracy of the instrument. |
| Matrix spikes | At least one per preparation batch or as indicated on COC. | Meet %R requirements as specified in the method. | Qualify data | Data Validator | Evaluate accuracy and representativeness accounting for the variability of sample matrix. |
| Matrix spike duplicates (except VPH, EPH, metals) | At least one per preparation batch or as indicated on COC. | Meet %R requirements as specified in the method. | Qualify data | Laboratory Analyst | Evaluate precision, accuracy and representativeness accounting for the variability of sample matrix. |
| Laboratory duplicate (VPH, EPH, metals only) | At least one per preparation batch or as Indicated on COC. | Meet %R requirements as specified in the method. | Qualify data | Laboratory Analyst | Evaluate precision, accuracy and representativeness accounting for the variability of sample matrix. |

TABLE B5-2 (CONTINUED)

LABORATORY QUALITY CONTROL

| Type | Frequency | Measurement Performance Criteria | Corrective Action (CA) | Person Responsible For CA | Data Quality Indicator |
|---|---|---|---|---|---|
| LCS | Minimum of 1 per analytical batch or per 20 field samples; whichever is less. | Meet %R requirements as specified in the method. | Check if MS/MSD acceptable to compare for matrix effects. Re-prepare and re-analyze associated samples to obtain acceptable LCS. | Laboratory Analyst | Evaluates accuracy |
| Performance Evaluation | 2 during course of program. | Supplied by APG: Within the 95% confidence interval, vendor supplier specified. | Re-prepare and re-analyze SRM %R. | Data Validator | Evaluates accuracy |
| Initial calibration | As specified in the method. | As specified in the method. | Re-calibrate; check system. | Laboratory Analyst | Establish instrument response and linearity. |
| Calibration check sample | As specified in the method. | 90-110% recovery for inorganics; as specified in EPA methods for organics. | Re-calibrate; check system. | Laboratory Analyst | Evaluate stability and accuracy of instrumentation. |
| Surrogate standards | Every sample, blank, standard prior to extraction. | As specified in the method. | Note %R which are outside limits in case narrative. If no obvious interferences, reextraction/analysis of sample required. | Laboratory Analyst | Evaluate accuracy of sample introduction and effect of matrix on analysis. |

TABLE B5-2 (CONTINUED)

LABORATORY QUALITY CONTROL

| Type | Frequency | Measurement Performance Criteria | Corrective Action (CA) | Person Responsible For CA | Data Quality Indicator |
|---|---|---|---|---|---|
| Internal standards | Every sample, blank, standard after extraction. | As specified in the method. | Note %R which are outside limits in case narrative. If no obvious interferences, reextraction/analysis of sample required. | Laboratory Analyst | Provide a standard of retention time and response which is invariant from run-to-run with the instruments. |

CA = Corrective Action
RL = Reporting Limit
R = Recovery
COC = Chain-Of-Custody
LCS = Laboratory Control Sample
MS/MSD = Matrix Spike/Matrix Spike Duplicate

## TABLE B8-1

## INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONSUMABLES

| Critical Supplies and Consumables | Inspection Requirements and Acceptance Criteria | Responsible Individual |
|---|---|---|
| Sample containers/lids | Visual inspection for cracks, breakage, etc. | Field Team Leader |
| Field Measurement Equipment | Functional checks to confirm calibration and operating capacity. | Field Team Leader |
| General supplies and spare parts | Inspect for obvious damage, functionality, etc. | Field Team Leader |
| Laboratory Disposable Equipment | Visual inspection for cleanliness and damage. | Laboratory Analyst |
| Colorimetric Gas Tubes | Inspect for damage, discoloration, ineligible markings and appropriate range. | Field Team Leader |
| Summa Canisters | Inspect for damage, confirm vacuum pressure and certified clean | Field Team Leader |
| Tedlar Bags | Inspect for cleanliness and damage | Field Team Leader |

# FIGURE B3-1

# EXAMPLE SAMPLE LABEL AND CUSTODY SEAL

| STL EDISON<br>a division of Severn Trent Laboratories, Inc.<br>777 New Durham Road<br>Edison, NJ 08817<br>(732) 549-3900 | | |
|---|---|---|
| Project Name/Client | | |
| Sample Location/Description | | |
| Test Parameters | | |
| Container No. | Preservative | |
| Date | Time | Sampler's Initials |

Custody Seal:

Date_____ Project_____

Signature_____ Container #_____of_____

Figure B3-2

Example Chain of Custody Record

| STL Mobile<br>900 Lakeside Drive<br>Mobile, AL 36693<br>phone 251-666-6633 fax 251-666-6696 | **Chain of Custody Record** | SEVERN TRENT STL<br>Severn Trent Laboratories, Inc. |
|---|---|---|

| Client Contact | Project Manager: | Site Contact: | Date: | COC No: |
|---|---|---|---|---|
| Your Company Name here | Tel/Fax: | Lab Contact: | Carrier: | _____ of _____ COCs |
| Address | Analysis Turnaround Time | | | Job No. |
| City/State/Zip | Calendar ( C ) or Work Days (W) _____ | | | |
| (xxx) xxx-xxxx Phone | TAT if different from Below _____ | | | SDG No. |
| (xxx) xxx-xxxx FAX | ☐ 2 weeks | | | |
| Project Name: | ☐ 1 week | | | |
| Site: | ☐ 2 days | | | |
| P O # | ☐ 1 day | | | |

| Sample Identification | Sample Date | Sample Time | Sample Type | Matrix | # of Cont. | Filtered Sample | | | | | | | | | | | | | | | | Sample Specific Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | |

**Preservation Used:** 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

| *Possible Hazard Identification* | *Sample Disposal ( A fee may be assessed if samples are retained longer than 1 month)* |
|---|---|
| ☐ *Non-Hazard* ☐ *Flammable* ☐ *Skin Irritant* ☐ *Poison B* ☐ *Unknown* | ☐ *Return To Client* ☐ *Disposal By Lab* ☐ *Archive For* _____ *Months* |

**Special Instructions/QC Requirements & Comments:**

| Relinquished by: | Company: | Date/Time: | Received by: | Company: | Date/Time: |
|---|---|---|---|---|---|
| Relinquished by: | Company: | Date/Time: | Received by: | Company: | Date/Time: |
| Relinquished by: | Company: | Date/Time: | Received by: | Company: | Date/Time: |

FIGURE B10-1
GROUNDWATER SAMPLING FIELD DATA SHEET


**Cornell-Dubilier Electronics Superfund Site**

## GROUNDWATER SAMPLING FIELD DATA SHEET

Well Number: _____

Sample I.D.: _____ (if different from well no.)

Project: _____ Job No.: _____ Date: _____ Time: _____

Personnel: _____ Weather Conditions: _____

Air Temperature: _____

### WELL DATA:

Water Level: ❑ Measured ❑ Historical

Casing Diameter: _____ ❑ Stainless Steel ❑ Galv. Steel ❑ PVC ❑ Teflon® ❑ Other: _____

Intake Diameter: _____ ❑ Stainless Steel ❑ Galv. Steel ❑ PVC ❑ Teflon® ❑ Open rock

DEPTH TO Static Water Level: _____ Bottom of Well: _____ Measured with:

DATUM: ❑ Top of Protective Casing ❑ Top of Well Casing ❑ Other: _____

Is the well clean to the bottom? ❑ Yes ❑ No Is the well in good condition? ❑ Yes ❑ No

VOLUME OF WATER: Standing in well: _____ To be purged:

### PURGE DATA:

Air Quality: Ambient Air:_____(ppm) Well Head:

METHOD: ❑ Bailer, Size: ____ ❑ Bladder Pump ❑ 2" Submersible Pump ❑ 4" Submersible Pump

MATERIALS: ❑ Teflon® ❑ Stainless Steel ❑ PVC ❑ Other: _____ Tubing/Rope: [ Teflon® [ Polyethylene [ Polypropylene [ Other: _____

Pumping Rate: _____ Elapsed Time: _____ Volume Pumped: _____

Was well purged to dryness? ❑ Yes ❑ No Number of Well Volumes Removed: _____

TIME SERIES DATA:

| | | | | | Decon. Fluids Used: |
|---|---|---|---|---|---|
| Well Volumes: | _____ | _____ | _____ | _____ | |
| Temp.: | _____ | _____ | _____ | _____ | ❑ Methanol |
| pH: | _____ | _____ | _____ | _____ | ❑ DI Water |
| Spec. Cond.: | _____ | _____ | _____ | _____ | ❑ Hexane |
| (ORP) Redox | _____ | _____ | _____ | _____ | ❑ HNO3 |
| Potential: | _____ | _____ | _____ | _____ | ❑ Potable Water |

PURGING EQUIPMENT: ❑ Dedicated ❑ Prepared Off-Site ❑ Field Cleaned

### SAMPLING DATA:

METHOD: ❑ Bailer, Size: ____ ❑ Bladder Pump ❑ 2" Submersible Pump ❑ 4" Submersible Pump

MATERIALS: Pump/Bailer: ❑ Teflon® ❑ Stainless Steel ❑ PVC ❑ Other: _____ Tubing/Rope: ❑ Teflon® ❑ Polyethylene ❑ Polypropylene ❑ Other: _____

SAMPLING EQUIPMENT: ❑ Dedicated ❑ Prepared Off-Site ❑ Field

Metals samples field filtered? ❑ Yes ❑ No Method:

APPEARANCE: ❑ Clear ❑ Turbid ❑ Color: _____ ❑ Contains LNAPL ❑ Contains DNAPL

FIELD DETERMINATIONS OF RECORD:

pH: _____ Meter Model: _____ Meter S/N:

Temperature: _____ Spec. Cond.: _____ _____

NO. OF CONTAINERS: ___ Field Blank I.D.: _____ Trip Blank I.D.: _____ Replicate I.D.:

REMARKS:

I certify that this sample was collected and handled in accordance with applicable regulatory and project protocols.

Signature: _____ Date: _____

FIGURE B10-2

# COLOR-TEC FIELD DATA SHEET

## CORNELL DUBLIER ELECTRONICS - OU3

| SAMPLE ID | DATE | ANALYST | DIRECT TUBE READING | TUBE RANGE (LL,L,M, HA) | PURGE VOLUME (CC) | CORRECTION FACTOR | CORRECTED TUBE READING | NOTES/COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |

# C ASSESSMENT AND OVERSIGHT

## C1 Assessments and Response Actions

The assessment and response actions for the field and laboratory activities are described in Sections C1.1 and C1.2. In addition to these actions, USEPA Region 2 may perform external audits, either announced or unannounced, at its discretion.

### C1.1 Field Assessment and Response Actions

Following completion of the field activities associated with each sampling event, the QA Officer will assess the work for the following items:

- Water levels were collected from the required monitoring well locations
- Water levels recorded in the database are consistent with the field notes (i.e., check for transcription errors) and previously recorded measurements
- Groundwater samples were collected from the required locations
- Field data sheets were correctly filled out for each sampling location
- Chain-of-Custody records were correctly completed
- Samples arrived at the lab properly packaged for shipment (i.e., temperature requirements were met and there was no breakage of sample containers)

Problems identified by this assessment will be noted and addressed as part of the data validation and usability discussed in Section D. The sampling team will be notified of any potential discrepancies, provided with additional guidance or examples of proper procedure as applicable, or reassigned as needed. If applicable, additional data collection efforts will be implemented (i.e., collect additional water levels or samples).

## C1.2 Laboratory Assessment and Response Actions

STL Edison's assessment and corrective actions approach is summarized below.

Each corrective action is thoroughly investigated, and the investigation, outcome of the investigation, action taken and follow-up, are documented. Corrective action reports are reviewed, approved, and maintained by the QA department.

### Initiation

Any employee is authorized to initiate a corrective action. The initial source of corrective action can also be external to the lab (i.e., corrective action because of client complaint, regulatory audit, or proficiency test). When a problem that requires corrective action is identified, the following items are identified by the initiator on the corrective action report: the nature of the problem, the name of the initiator, and the date. If the problem affects a specific client project, the name of the client and laboratory project number is recorded, and the PM is informed immediately.

### Cause Analysis

The corrective action process must be embarked upon as a joint, problem solving, constructive effort. Identification of systematic errors, or errors that are likely to occur repetitively due to a defect or weakness in a system, is particularly valuable in maintaining an environment of continuous improvement in laboratory operations.
When a corrective action report is initiated, the initiator works with the affected employee(s) and/or department(s) to identify the root cause of the problem. An essential part of the corrective action process is to identify whether the problem occurred due to a systematic or isolated error.

If the initiator of the corrective action report is uncertain as to what would constitute appropriate corrective action or is unable to resolve the situation, the problem is identified to the Supervisor, Manager, Laboratory Director or the QA Manager who provides assistance in the corrective action process.

The root cause of the problem and associated cause analysis is documented on the corrective action form.

## Corrective Action

Once the root cause of a problem is identified, the initiator and affected employee(s) and/or department(s) examine potential actions that will rectify the present problem to the extent possible, and prevent recurrence of future, similar occurrences. An appropriate corrective action is then recommended. The corrective action must be appropriate for the size and nature of the issue.

Corrective action must be completed before the data is released. Implementation of the corrective action and the date of implementation are documented on the corrective action report.

If a corrective action is related to a specific project report, included in the project file. An essential part of the corrective action process is communication and awareness of the problem, the cause, and the action taken to prevent future occurrences and/or rectify the immediate problem.

## Monitoring Corrective Action

Corrective action reports are maintained by the QA Department. The QA department reviews corrective actions and selects one or more of the more significant corrective actions

for inclusion in the annual systems audit. The QA Department also may implement a special audit. The purpose of inclusion of the corrective action process in both routine and special audits is to monitor the implementation of the corrective action and to determine whether the action taken has been effective in overcoming the issue identified.

**Preventive Action**

Preventative action is defined as noting and correcting a problem before it happens, because of a weakness in a system, method, or procedure. Preventative action includes analysis of the Quality System to detect, analyze, and eliminate potential causes of non-conformances. When potential problems are identified, preventative action is initiated to effectively address the problem to eliminate or reduce the risk identified. The preventative action process takes the same format as the corrective action process.

## C2 Reports to Management

### C2.1 Field Activities Report

The results of the field assessment described above will be reported to the Project Manager on a quarterly basis. The Project Manager will confirm that any issues have been discussed with the sampling team, that the team has the most current documents available, and/or that they are prepared to collect the required information during the next sampling event. The Project Manager will also be responsible for assigning alternative or additional staff as needed.

### C2.2 Laboratory Analysis Report

Formal quality assurance reports from the Laboratory Quality Assurance Manager will be submitted to the appropriate management personnel (Project Manager, Task Manager, Project Quality Assurance Officer, Technical Director, or Laboratory Director) as needed if a change in the QA/QC Program occurs, or to document the results of a corrective action.

An audit report will be submitted to the Laboratory Director as a result of either an internal or external laboratory audit.

There are several types of internal audits performed during the year. At least two complete system audits are scheduled each year along with a random number of method audits. Internal blind quality control samples are dispersed into various areas of the laboratory to evaluate specific analyses' performance. Internal audit reports are submitted by the Quality Assurance Manager to the Laboratory Director for initial review. Audit reports are then forwarded to the appropriate Section Manager for their evaluation and to respond to documented deficiencies.

External on-site system audits and Performance Evaluation Studies (WP and WS) are conducted routinely by City, State and Federal Agencies or major client representatives. The audit report is submitted to the Quality Assurance Manager/Laboratory Director by the external audit source. The audit report is forwarded to the Section Managers for evaluation and response to deficiencies cited. The response to deficiencies discovered by external audits is dependent upon the auditor's requirements. The response is submitted to the Quality Assurance Manager and Laboratory Director by the Section Manager for review before implementation of the corrective action plan is initiated. The information of the external audit is maintained by the laboratory.

# D DATA VALIDATION AND USABILITY

## D1 Data Review, Validation, and Verification Requirements

Data will be validated to verify that the project DQOs were met. Analytical validation will be conducted as described below and the laboratory will maintain full quality assurance and quality control documentation that will be available upon request.

## D2 Validation and Verification Methods

### D2.1 Field Data Validation and Verification

The evaluation of field information will include checking for transcription errors, review of field notes, and verification that required field measurements and samples were obtained and that the work was completed in accordance with the applicable SOP. Subsequent hydraulic and water quality events will be compared to data previously obtained. The Field Team Leader will perform these reviews under the Supervision of the QA Manager.

### D2.2 Laboratory Data Validation and Verification

Final analytical data generated during this investigation will be validated in accordance with USEPA Region II SOPs as described below. Analytical data generated from the field screening samples, however, will not be subject to data validation as these data are intended for screening purposes only. The final analytical data packages generated during this investigation, excluding data generated from the field screening samples, will be validated in accordance with the current USEPA Region II SOPs for SW-846 methods (available at http://www.epa.gov/region02/smb/sops.htm). These will include HW-24, Revision 1, June

1999, HW-22, Revision 1, April 1995, and HW-23, Revision 0, May 1995. CLP data validation methods for inorganics, HW-2, Revision 11, January 1992 will also be employed, using best professional judgment as applicable to SW-846 methodology.

Upon completion of the data validation process, a summery report for each analysis parameter/data package will be prepared. Data summary tables and annotated Form Is will be included with the report as attachments. The written report will not include preparation of the USEPA Region II Checklist forms, as software programs will be used for verification of mathematical calculations as opposed to manual entries on the Checklist.

The Data Validation will also determine the overall completeness of the data package. Completeness checks will be conducted on the data to determine whether deliverables specified in the FSP/QAPP Section B10.2, are present. In addition, the analytical data will be verified in the context of the data usability. For example, the data validation may indicate that one or more detection limits were higher than called for in the FSP/QAPP. Although this discrepancy will be called out as part of data validation, the detection limits may still be below the applicable regulatory standard. In this example, the data would still be usable for its intended purpose. Conversely, if the detection limits were above the standard, the data may not be suitable for its intended purpose or may be managed through the risk assessment as described in Section A7.1. Such conditions would also be noted as applicable.

## D3 Reconciliation with Data Quality Objectives

As noted in Section A7, the collected data must be sufficient to determine and confirm the presence or absence of constituents in groundwater above their respective MCLs or New Jersey Groundwater Quality Standards (NJGWQS), or in the absence of established MCLs or NJGWQS, a Risk Based Concentration. For soil gas and indoor air, the data must be sufficient to determine and confirm the presence of constituents above the applicable soil gas or indoor air criteria. Therefore, the first step in the data reconciliation will be to compare the achieved detection limits for each analyte to its respective MCL, NJGWQS, or a Risk Based Concentration. If a detection limit is greater than these criteria, the associated

constituent will be included for further evaluation as a possible COPC in the risk assessment. To assess the appropriateness of including each constituent, the risk assessment will consider the likelihood that a constituent is present below the detection limit (e.g. daughter product, historical information) and the weight of evidence on the toxicity of the constituent (e.g., Class A carcinogens will be given high priority for inclusion as a COPC).

The collected data will also be evaluated spatially from both a horizontal and vertical perspective. In this manner, the effectiveness of the collected data in meeting the data quality objective of defining the extent of off-site impacts to groundwater can be evaluated.

Finally, the data will be evaluated for evidence of natural degradation of the site constituents and environmental conditions that may be favorable to continued degradation. This will include the evaluation of ratios of parent compounds to daughter products, source and/or historical concentrations to downgradient and/or recent data, presence of reducing or oxidizing conditions, etc. This will further assist in defining the extent of off-site impacts to groundwater.

# APPENDIX A
# GROUNDWATER SOP's


Environmental
Engineers & Scientists

# GROUNDWATER SAMPLING SOP

# GROUNDWATER SAMPLING
# STANDARD OPERATING PROCEDURE

## Well Purging Procedures

Before collecting a representative groundwater sample, monitoring wells will be purged in accordance with the U.S. Environmental Protection Agency-Region II Standard Operating Procedure "Groundwater Sampling Procedure Low Stress (Low Flow) Purging and Sampling" (March 16, 1998), included as an attachment to this SOP. Groundwater wells will be purged at a rate of 200 to 500 ml per minute until three consecutive indicator readings are within the following ranges of each other:

± 0.1 for pH

± 3% for conductivity

± 10 mv for redox potential (ORP)

± 10% for DO and turbidity

Should poor recovery be an issue, the well will be pumped and allowed to recover until a sufficient volume has flowed into the well for sampling. Pumping rates will be adjusted depending upon the recovery rate of each well.

Equipment List (Typical):

- Grundfos Redi-flo2 Submersible Pump (bladder pump for Dissolved Hydrogen sampling)
- 3/8" polyethylene dedicated tubing
- Field instrumentation (PID and Horiba or equivalent)
- Field logbook
- Monitoring well lock keys
- Water level indicator
- Graduated bucket

1 Unlock the well cover and carefully remove it to avoid having foreign material enter the well. Monitor the interior of the riser pipe for organic vapors using a photoionization detector. If a reading of greater than 5 ppm is recorded, vent the well until levels are below 5 ppm before pumping is conducted.

2 Using an electronic water level indicator, measure the water level below top of casing (from permanent marked point).

3 Decontaminate the water level indicator between each monitoring well as outlined in the Decontamination SOP.

4 Measure and cut a length of 3/8" polyethylene tubing equal to the total casing length plus 5 feet. Secure tubing to the pump and electrical leads. Insert secured pump into well casing to the middle of the screened interval.

5 Begin evacuation. Monitor the water level drawdown adjusting pumping rate to maintain equilibrium between recharge rate and evacuation rate, if possible. Continue pumping until the field indicator parameters are stabilized. If the recharge rate is not sufficient to maintain equilibrium with the extraction rate, such that the water level drops in excess of one foot, gently (to minimize generation of turbidity) lower the pump as needed to evacuate the well.

6 Every five minutes collect indicator readings for the parameters listed above.

7 Collect well purge water for appropriate disposal.

8 Close protective cap and lock protective casing.

9 Record well purging data in the field logbook.

## Groundwater Sampling Procedures

The first round of groundwater monitoring well sampling will be performed a minimum of two weeks after the development of each set of groundwater monitoring wells. Well sampling will be performed on the same day as purging of the well, after the well has recovered sufficiently to sample, preferably within two (2) hours after evacuation. The only exception to the two (2) hour criterion will be for those slow recovery wells where insufficient sample has accumulated to sample within the required two hours. For these wells, sample collection will take place as soon as the required sample volume can be feasibly collected.

1 Immediately after the field parameters reach stabilization, or within two (2) hours of monitoring well purging, if the well has recharged enough to sample, samples will be collected into appropriate containers using the pump and dedicated tubing used to purge the monitoring well.

2 Collect groundwater sample in appropriately prepared (I-Chem Series 300 or equivalent) containers (containing appropriate preservatives, if required) directly from pump discharge tube. Samples for VOC analysis should be filled first, leaving no head space in the VOA container. All other containers should be filled to the shoulder of the container.

3 Record well sampling data on the Groundwater Sampling Field Data Sheet (enclosed at the end of this attachment).

4 Close and lock protective casing.

5 Label each sample container with the appropriate sample identification data and place in coolers for transport to the analytical laboratory.

6 Initiate standard chain-of-custody procedures.

## Groundwater Sample Collection with the Water FLUTe System

Groundwater sample collection at wells completed with the Water FLUTe will be completed in accordance with the enclosed manufacturer's instructions. Compressed nitrogen gas will be used to apply pressure to the large (½ inch diameter) portion of the U tube (See Figure in enclosed vendor literature) at sufficient pressure to purge the tube of water (purge pressures are provided by the manufacturer for each Water FLUTe but are typically on the order of 100 psi). The pressure is then released and the tube is allowed to fill back up with formation water. This procedure is completed twice, releasing the pressure between purge volumes in order to allow the U tube to fill with formation water. The pressure is then reduced (value provided by the manufacturer) and applied a third time during which the sample is collected from the slender portion of the U tube as it flows to the surface. The first 0.75 to 1 gallon of purge water is discarded prior to sample collection. The sample is driven to the surface by the displacement of water in the large portion of the U tube and does not come into contact with the compressed nitrogen. The samples are then labeled and handled in the same manner as those collected from the monitoring wells.

# COLOR-TEC FIELD SCREENING SOP

# Color Tec Screening Method (CTSM) for Analysis of Total Chlorinated Compounds in Groundwater STANDARD OPERATING PROCEDURE

## TABLE OF CONTENTS



## LIST OF TABLES



## LIST OF FIGURES

# 1.0 OBJECTIVE

The objective of the Color Tec Screening Method (CTSM) is to provide semi-qualitative and relative order of magnitude total chlorinated compound concentrations in groundwater samples. These data will be used to assist in field decision making related to installation of intermittent casings and the depth at which to terminate drilling activities at a given borehole location.

The objective of this SOP is to establish consistent and technically defensible procedures for the field analysis of groundwater samples using the CTSM. This standard addresses both the theory and specific field procedure for application of the method. The theoretical considerations regarding the method are described in Section 3. Specific "how to" instructions for implementation of the CTSM on groundwater sampling programs are presented in Section 4.

# 2.0 APPLICABILITY

This standard will be used for the development of groundwater screening data by the CTSM. The purpose of the Color-Tec method is to provide fast, low-level, low cost, decision-quality data to determine the presence-or-absence (i.e. qualitative) of total chlorinated compounds at or below regulatory levels in groundwater and soil.

# 3.0 TECHNICAL BACKGROUND

## 3.1 Method Description

The Color-Tec method combines standard, commercially available colorimetric gas detector tubes with a unique sample purging technique. This is achieved by using a hand-operated vacuum pump to purge the volatile compounds from a groundwater or soil sample through the colorimetric tube, which is designed to produce a distinct color change when exposed to chlorinated compounds (Figure 1). Each colorimetric tube contains an oxidizer that decomposes the chlorinated compounds entering the tube, releasing hydrogen chloride, which discolors the reagent in the tube. Calibration

scales printed on the detector tubes facilitate measurement of the linear extent of the color change reaction that occurs within the tube. The tubes react positively to all chlorinated alkenes, and (to a slightly lesser degree) to the chlorinated alkanes. Therefore, the total response indicated by the detector tube reflects the sum of the concentration of each individual chlorinated compound present in the sample. In comparisons of the colorimetric tube readings to the pre-prepared standards, the method routinely detected tetrachloroethene (PCE) and vinyl chloride at concentrations of 1 micrograms per liter (µg/L) and below. In comparisons using the field-generated data, Color-Tec routinely detected total chlorinated compounds at or below the regulatory levels of the specific compounds detected by gas chromatograph/mass spectrometer (GC/MS) analysis in the duplicate samples (including PCE ≤5 µg/L, trichloroethene [TCE] ≤5 µg/L, and vinyl chloride ≤2 µg/L).

The colorimetric detector tubes are constructed of glass and printed with calibration scales to facilitate measurement of the linear extent of the color change reaction that occurs within the tube. To conduct the method with a groundwater sample, a standard 40-milliliter (ml) volatile organic analysis (VOA) vial is filled with the sample to approximately 70% capacity (leaving a 30% headspace) and tightly capped. The sample vial is then heated to approximately 40 degrees Celsius (°C) in a water bath (Figure 2).

After the vial is heated, the headspace within the sample vial is connected to the colorimetric tube via a hollow, steel extraction needle attached to a short piece of Tygon® tubing. A second, hollow, steel purge needle is inserted through the septa to the bottom of the VOA vial to facilitate purging. Using a manual vacuum pump (Figure 1), approximately 100 to 150 cubic centimeters of ambient air is purged through the water sample within the VOA vial directly into the colorimetric gas detector tube (no water is to enter the colorimetric tube – only purge-air and contaminant vapors). The purging process requires 60 to 90 seconds to strip most of the volatile compounds from the sample.

Colorimetric Tubes

The tube manufacturer provides tubes for a variety of concentration ranges. Initially, the lowest concentration range tube is used to analyze the sample. When a positive result is observed, the concentration level is obtained by matching the linear extent of the discolored reagent inside the tube to the calibration scale printed on the outside of the tube. If the calibrated range of the tube is

exceeded by the initial reaction, a tube with a higher concentration range is used to analyze a duplicate sample. This procedure is repeated until the approximate concentration is determined.

It should be noted that the chlorinated compounds containing fewer chlorine molecules (such as vinyl chloride) induce a weaker reaction in the tubes than those compounds containing more chlorine molecules (such as PCE). Therefore, when a sample contains only vinyl chloride, additional sample volume and purge volume may be required to achieve the same color reaction as when the sample contains PCE. It is important to note that because the colorimetric tubes react to all chlorinated compounds, specific chlorinated species cannot be distinguished using this method. Therefore, the values observed using the method reflect the sum of the concentration of each individual chlorinated compound present in the sample.

Tube Temperature

The detector tubes are designed to operate at temperatures between 0 and 40°C (32 to 104° Fahrenheit [F]) and are calibrated based on a tube temperature of 20°C (68°F). When the sample and/or the tube are above 20°C, the tube's sensitivity to the targeted compounds is increased. Conversely, when the sample and/or the tube are below 20°C, the tube's sensitivity to the targeted compounds is decreased. Therefore, to maximize the detection capability of the colorimetric tube, the samples and tubes should be heated to approximately 40°C before beginning the purging process.

Potential Limitations

The Color-Tec method is intuitively simple to operate, requiring minimal practice to master. As with any analytical method, however, there are limitations that must be considered by the user to effectively apply the method to the intended use while avoiding the collection of unrepresentative data.

Possible Interference Compounds

Bromine, free chlorine, and hydrogen chloride can indicate a positive reaction in the colorimetric tubes. These compounds, however, are not likely to be present at most sites at sufficient levels to interfere with the detection of chlorinated compounds using the method. False-positive reactions could potentially occur if the water sample being analyzed was preserved with hydrochloric acid

(HCl); therefore, VOA bottles pre-preserved with HCl should be avoided. The colorimetric tubes detect all chlorinated compounds present in the sample. This interference from the other chlorinated compounds makes the identification of a specific chlorinated compound within the sample impossible.

The presence of toluene or xylenes in a sample reduces the colorimetric tube's sensitivity to chlorinated compounds. Therefore, the Color-Tec method is not recommended for use in areas where petroleum compounds are suspected or
known to be present with the chlorinated compounds being targeted.

Subtle Positive Color Change Response at Low Concentrations

When a sample contains very low concentrations (<10 µg/L) of chlorinated compounds, the resulting color change is not immediate or distinct. At these low concentrations, the color change does not usually begin until 100 to 150 cubic centimeters of air have purged through the sample. Furthermore, the color change induced at these low concentrations is very slight (below 0.5 on the tube scale) and appears as a slight darkening or light purple hue at the entrance of yellow reagent layer in the low-level tube. The solution to this problem is careful examination of each tube during and after purging.

Water Vapor

A build-up of water vapor in the tube past the catalyst stage can induce a subtle color change similar to that of a low level positive result. This problem is easily avoided by observing the build-up of condensation in the black catalyst stage of the tube during purging, and stopping the airflow when the condensation nears the end of the catalyst stage. The sample will most likely be thoroughly purged by the time this occurs.

Interrupted Air Flow

Thorough purging of the sample is critical for low-level detection. Therefore, the user must recognize and correct any problem that would decrease or interrupt the airflow through the sample and the detector tube, such as clogged needles and bad pump seals.

Airborne Contaminants

Because the method uses ambient air as the purge gas, airborne chlorinated compounds at low concentrations can enter the sample and activate the detector tube. The method may be used with a carbon pre-filter attached to the purge needle to prevent airborne contaminants from entering the sample and detector tube during sample purging and analysis. This modification is most useful during site investigations at or near active facilities (such as dry cleaner sites and active industrial facilities) where contaminants may be released into the ambient air. The carbon pre-filter is a small, disposable glass tube packed with coconut shell charcoal (CSC). The carbon pre-filter is attached to the purge needle using a small section of tubing and a luer fitting. At most sites, a single pre-filter tube may be reused for several sample purges. However, at sites where high concentrations of airborne chlorinated compounds are suspected in the ambient air, the pre-filter tubes should be changed more frequently.

## 4.0 SAMPLING PROCEDURES

Sample Preparation

Water: Collect the water sample directly from the sampling device into three 40ml VOA vials by filling to ~70% capacity (i.e. to about 1-inch below the shoulder of the vial). Tightly secure the cap onto the partially-filled VOA vials. If duplicate samples are to be collected for possible laboratory analysis, collect these samples at the same time and store them on ice pending shipment to the laboratory. (note: samples for laboratory analysis should not contain any head space)

**Important Note:** The VOA vial containing the water sample to be field tested must contain an air-filled headspace to accommodate purging. Do not use VOA vials preserved with HCL.

Three VOA vials will be prepared for each sample to be tested. The additional VOA vials may be used in either of the following situations:

- When the initial test does not induce a color change in the colorimetric tube, the second bottle containing a duplicate sample, may be purged using the original colorimetric tube to increase the probability of detecting very low (<10µg/L) concentrations.

- When the initial test induces a color change that exceeds the upper limit of the LL tube, the extra bottle(s) can be used to analyze the sample using higher range colorimetric tubes (L, M, HA) to tentatively quantify the higher concentrations of chlorinated compounds.

Heating Samples and Tubes (Figure 2)

Connect hot plate to a power source and switch it on (refer the hot plate manufacturer's manual for complete operation instructions). Place the test tube rack into the steel pan, fill the pan ¾ full of water and place the pan onto the hot plate. Place the thermometer into the water and adjust the hot plate, control knob to heat the water to the desired temperature. Samples should not be heated in excess of 100°F: although, the water in the pan may be heated to above 100° F to facilitate faster heating of the sample. Both the test vials and the colorimetric tubes should be heated to 100° F.

## 4.1 Purge and Analysis Procedure

Set-Up and Operation

(Refer to Figure 1 for equipment identification)

1. Break both glass tips of an LL tube.
2. Attach the colorimetric tube to an extraction needle assembly by inserting the clear end of the glass tube into the open end of the clear tubing.
3. Insert the yellow end of the colorimetric tube into the tip of the Gastec hand pump.
4. Place a sealed VOA vial, containing pre-heated sample water, into the bottle holder on the pump stand.
5. Insert the extraction (short) needle into the septa of the VOA vial. Be sure that the tip of the extraction needle is positioned within the headspace of the VOA vial (above the water level).
6. Insert a purge (large) needle into the septa of the VOA vial, and push the tip of the needle below the water level as far into the vial as possible.
7. If carbon filtration of the ambient air is required, attach a carbon filter assembly to the luer fitting on the top of the purge needle. (See carbon filter assembly set-up procedure)
8. Pull pump handle out and lock in place at the 50cc position. (For complete hand pump operation instructions please refer to the Gastec hand pump manual)

9. Observe the sample in the VOA vial to determine if air bubbles are flowing from the tip of the purge (long) needle through the sample. Air should be flowing (bubbling) through the sample. If air is not flowing through the sample, one of the following problems may have occurred:
   - Clogged/blocked purge (long) needle (most common cause of flow problems);
   - Colorimetric tube is not securely connected to hand pump;
   - Colorimetric tube is not securely connected to extraction needle tubing;
   - Broken/bad seal in hand pump; and/or Clogged/blocked extraction (short) needle (least common cause of flow problems)

When the pump handle is locked open at the 100cc position, purging should continue through the sample for ~60 seconds. If the 100cc purge cycle ends (bubbling stops) before ~60 seconds have elapsed, the pump may require servicing.

Analysis

Samples may be purged using 50cc, 100cc, or 200cc purge volumes. These various purge volumes are used in succession to maximize the low-level detection rage of each tube, thereby reducing the number of tubes needed to tentatively quantify the concentration of total chlorinated compounds in the sample.

50cc Purge: Initially, samples are analyzed using an LL tube with a 50 cc purge cycle, unless existing data suggests higher concentrations are present (i.e. previous results, PID readings, etc.). If the concentration in the sample exceeds the upper detection limit of the tube (i.e the color change moves beyond the upper limit of the calibration scale printed on the tube), repeat the analysis using duplicate samples and higher range tubes (L, M, or HA) until the color change reaction stops within the calibration scale on the tube. Read the interface in the tube and use the pump stroke correction factors (provided below) to determine the correct reading for a 50cc purge volume. If the color change reaction exceeds the upper limit of the calibration scale or the HA tube, the sample contains a concentration of chlorinated compounds above the detection capability of the Color-Tec method.

100cc Purge: Following completion of the 50cc purge, if the concentration in the sample has induced a color change in the tube which traveled less than half the distance of the calibrated portion of the reagent phase of the tube, pull the pump handle outward and lock it into the 100cc

position to complete a full purge cycle. Record the value aligned with the stained/unstained interface on the tube. No correction factor is needed for a 100cc purge.

200cc Purge: Following completion of the 100cc purge cycle, if the concentration in the sample has induced only a slight (<0.5) color change reaction or no color change reaction, replace the original sample with a pre-heated duplicate sample and repeat the 100cc purge cycle using the original colorimetric tube.

Note: To replace the sample prior to the second 100cc purge cycle, remove both needles from the original VOA vial while the extraction needle tubing remains attached to the original colorimetric tube. Replace the original sample bottle on the pump stand with the duplicate sample bottle and immediately insert both needles into the septa of the duplicate sample bottle. With the duplicate sample bottle attached to the purge assembly, temporarily remove the colorimetric tube from the tip of the hand pump and re-insert the pump handle completely into the pump while the tube is un-attached. Re-attach the colorimetric tube into the pump tip. DO NOT replace the colorimetric tube prior to the second 100cc purge cycle—this MUST be the same tube used during the first 100cc purge of the original sample.

Read the calibration scale value aligned with the stained/unstained interface in the tube and use the pump stroke correction factors provided on the colorimetric tube instruction sheets (Table 1 below) to determine the correct reading for a 200cc purge volume.

## 4.2 Reading the Tubes

Once purging has been initiated, carefully observe the yellow reagent layer in the colorimetric tube (Figures 3 and 4).

Very Low Concentrations: When a sample contains very low concentrations (<10µg/L) of chlorinated compounds, the resulting color change is not immediate or distinct. At these low concentrations the color change does not usually begin until 70 to 90 CCs of air have purged through the sample. Furthermore, the color change induced at these low concentrations is very

slight (below 0.5 on the tube scale) and appears as a slight darkening or light purple hue at the entrance of yellow reagent layer in the LL tube (Figure 5).

Low to Medium Concentrations: When the sample contains higher concentrations (>10µg/L) of chlorinated compounds, the resulting color change is an obvious light to dark purple, which propagates through the yellow reagent layer toward the pump end of the colorimetric tube. The detected concentration level is obtained by matching the linear extent of the discolored reagent inside the tube to the calibration scale printed on the outside of the tube.

High Concentrations: When the sample contains high concentrations (>100µg/L) of chlorinated compounds, the color change reaction occurs quickly and usually exceeds the upper detection level of the LL tube. The higher the concentration of chlorinated compounds in the sample, the faster the color change reaction occurs and the further it propagates through the colorimetric tube. Samples containing percent-range concentrations (>1000µg/L) of chlorinated compounds, often discolor the entire yellow reagent layer in the LL tube before the pump handle has been fully extended. In these cases, the purging can be discontinued to allow for the current sample bottle to be re-tested using a higher range detector tube. There is no need to continue purging the sample when the detection level of the tube is exceeded. Each subsequently higher range tube is used to purge each new duplicate sample in succession until the color change reaction does not exceed the calibration range of the tube being used.

### 4.3 Recording Tube Readings

The tube readings and other pertinent field analysis information will be recorded on the data sheet illustrated in Figure 6. This includes the sample ID, the direct tube reading, the range of the colorimetric tube (LL, L, M, or HA), purge volume, the correction factor from Table 1 below, and the final corrected concentration. The sample ID will consist of the sample location and depth interval at which the sample was collected. For example, if the sample was collected from monitoring well location A at a depth of 130 to 140 feet, the sample ID would read "MW-A-130-140".

Pump stroke correction factors for the 133 series tubes are presented on Table 1 below.

## Table 1. Pump-stroke Correction Factors for 133-Series Tubes

| Tube | Purge Volume | Correction Factor |
|---|---|---|
| LL | 50 cc | Tube Reading x 3 |
| LL | 100 cc | Tube Reading x 1 |
| LL | 200 cc | Tube Reading ÷2 |
| | | |
| L | 50 cc | Tube Reading x 3 |
| L | 100 cc | Tube Reading x 1 |
| L | 200 cc | Tube Reading ÷2 |
| | | |
| M | 50 cc | Tube Reading x 2.5 |
| M | 100 cc | Tube Reading x 1 |
| M | 200 cc | Tube Reading ÷2.5 |
| | | |
| HA | 50 cc | Tube Reading x 3 |
| HA | 100 cc | Tube Reading x 1 |
| HA | 200 cc | Tube Reading ÷3 |

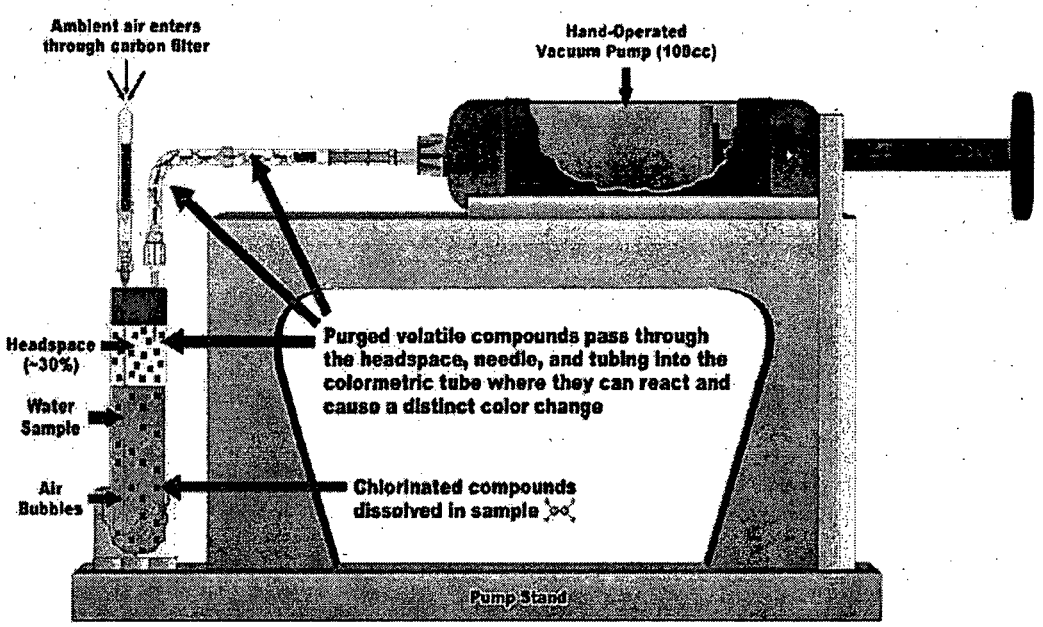



Figure 1. Test Assembly

Figure 2. Hot Plate And Test Vial Bath

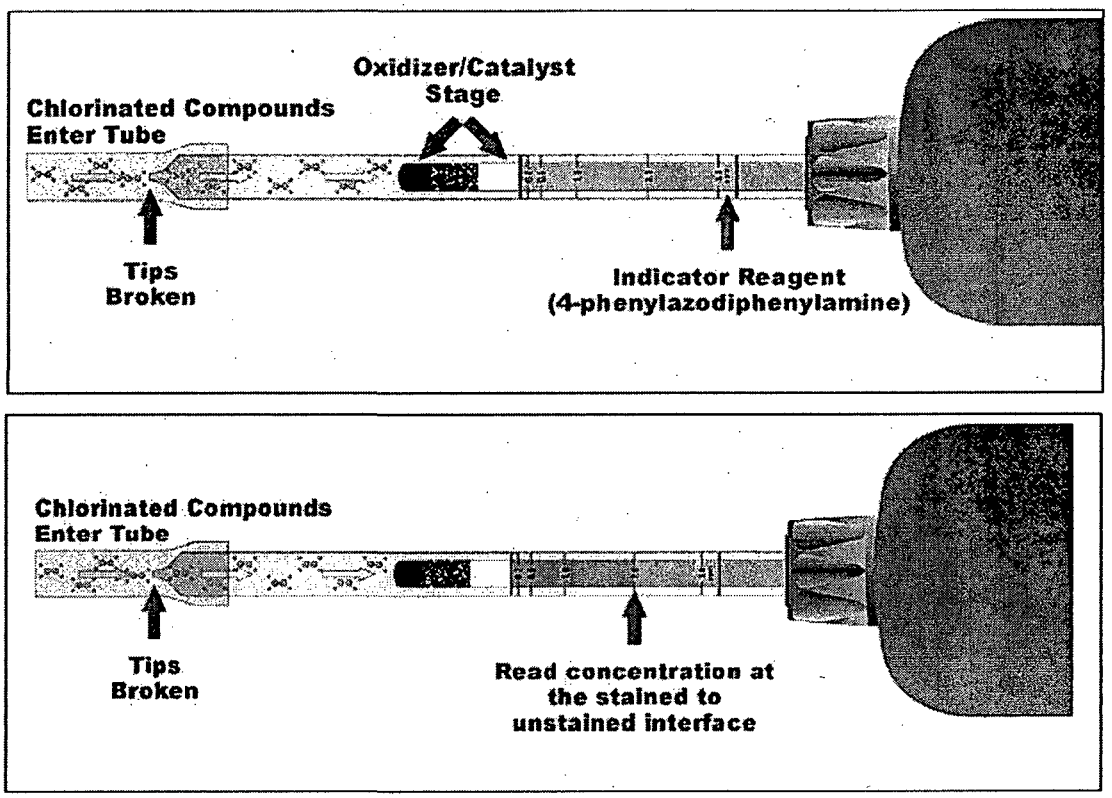



Figure 3. and Figure 4. Tube Readings

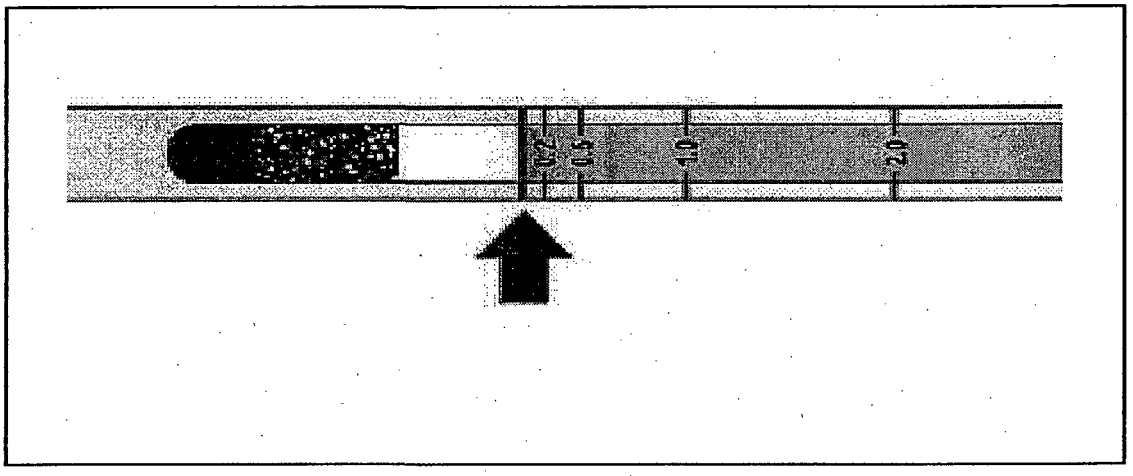


Figure 5. Low Level Tube Readings

FIGURE 1

# COLOR-TEC FIELD DATA SHEET

## CORNELL DUBLIER ELECTRONICS - OU3

| SAMPLE ID | DATE | ANALYST | DIRECT TUBE READING | TUBE RANGE (LL,L,M, HA) | PURGE VOLUME (CC) | CORRECTION FACTOR | CORRECTED TUBE READING | NOTES/COMMENTS |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |

# DISCRETE INTERVAL PACKER SAMPLING SOP

# DISCRETE INTERVAL PACKER SAMPLING STANDARD OPERATING PROCEDURE

Packer sampling is a method of obtaining representative water samples from a discrete interval within an open bedrock hole. The apparatus for this test consists of two inflatable rubber packers, a 2-inch submersible pump, and associated discharge tubing. The 2-inch submersible pump will either be mounted between the two inflatable rubber packers, or lowered through the assembly to immediately above the upper packer. If the latter method is used, a ten foot length of perforated steel pipe will be fixed between the two packers.

- Between boreholes and after having installed an intermediate casing, the packer equipment, steel pipe, submersible pump, and any other equipment placed into the boring will be decontaminated according to the procedures included in the Decontamination SOP.

- As placement of the packer assembly is established, field measurements of the apparatus will be made to ensure proper placement within the intended sample interval.

- Packer inflation is established.

- Water levels above the upper packer will be monitored to ensure a proper packer seal during purging and sampling.

- Purging will be accomplished in two stages. Initially, 10 volumes of the fixed 10 foot sampling interval will be purged to facilitate removal of the borehole water and collection of a representative sample of formation water. The pumping rate will then be lowered to 500 mL/min or less until the amount of water equal to the volume contained in the discharge tubing is evacuated. The groundwater sample will then be collected directly from the discharge tubing into the appropriate sample vial.

- In the event that the selected interval yields less than one gallon per minute, and at the discretion of the site Hydrogeologist, the packers may be deflated and moved to an alternative depth within the borehole. The objective is to locate an interval that produces sufficient volume so that a representative sample can be collected. Intervals that yield low volumes of water have a greater probability of cross contamination from the open borehole prior to sealing off the selected interval. Purging activities should not exceed approximately 30 minutes per location.

- Record the rate and total volume purged from each interval.

- Purge water will be collected for proper disposal.

# PACKER PRESSURE TESTING SOP

# PACKER PRESSURE TESTING
# STANDARD OPERATING PROCEDURE

Packer testing (permeability pressure testing) is a method of estimating the hydraulic conductivity of isolated bedrock zones within a borehole. This method will be used to identify zones of higher and lower hydraulic conductivity to assist in the selection of casing depths and monitoring intervals. The apparatus for this test consists of a perforated pipe positioned between two inflatable rubber packers. The packer pressure test interval is ten feet measured between the base of the upper packer and the top of the lower packer. The packers are inflated with compressed nitrogen from the ground surface to seal off the test interval from the remainder of the borehole. Potable water is pumped from the ground surface at a constant, known pressure into the isolated packer test interval. The volume of water pumped is then measured through time and recorded. The water volume that enters the bedrock under the specified pressure is a function of the hydraulic conductivity. An assembly of gauges at the ground surface controls water pressure and records volume pumped. The observed values are recorded on the appropriate field data form every minute for five minutes and are related to hydraulic conductivity, K, by the following equation:

$$K = C_p \frac{Q}{H}$$

Where: K = hydraulic conductivity (ft/year)
Q = rate of flow developed at equilibrium (gpm)
$C_p$ = packer coefficient (1/ft)
H = total calculated head (ft)

The packer coefficient consists of a shape factor that accounts for test section length, borehole diameter, and a unit conversion factor (gallons to $ft^3$ and minutes to years). This value is obtained from a standard table provided in the guide Earth Manual (Bureau of Reclamation, 1963).

The maximum pressures to be used during the test will be determined prior to testing by multiplying the depth of the top of the test interval below ground surface (i.e., the thickness of the overlying soil and rock) by a factor of 0.7. This value, in pounds per square inch (psi), will be the maximum

pressure applied during the test at that interval. Higher pressures have the potential to "lift" the tested rock, thus providing unrealistic values. For example, if the top of the test interval is 10 feet below ground surface, a pressure of 7 psi will be applied during the test.

Materials will be provided by the drilling subcontractor, and the tests will be conducted under the observation of a qualified hydrogeologist or environmental technician who will be responsible for recording the data and appropriately conducting the test. The hydraulic pressure test field data sheet is attached to this SOP.

The test will proceed as follows:

1. Lower the packer assembly to the selected test interval and inflate the packers.
2. Measure and record the water level in the borehole above the upper packer.
3. Record the diameter of the borehole.
4. Measure and record the water level in the interior of the pipe attached to the packers (i.e. the water level in the interval being tested)
5. Measure and record the height of the top of the injection pipe (the swivel) above ground surface. This is used to calculate the total static head of water above the test interval after the pipe is completely filled with water.
6. Connect the water lines and begin injecting water into the test interval at the selected pressure. Adjust the rate at which the water is injected into the test interval until flow rate and pressure stabilize.
7. Record the initial totalizer reading on the flow gauge and the pressure at which the water is being injected into the test interval.
8. Record these values at one minute intervals for five minutes.
9. Disconnect the water hose and gauges and remove packer assembly.

# Hydraulic Pressure Test
# Field Data Sheet

**Boring No.:**

| | |
|---|---|
| Project: **Cornell-Dubilier Superfund Site** | Sheet No. |
| Client: **Cornell-Dubilier Superfund Site PRP Group** | Job No. |
| Contractor: | Elevation: |
| Inspector: | Date: |

| Nominal Depth Upper Packer (ft) | Nominal Depth Lower Packer (ft) | Test Length Interval (ft) | Height Swivel/Gauge (ft) | Diameter of Drill Hole (ft) | (in) | Depth to Static Water Level (ft) |
|---|---|---|---|---|---|---|
| | | | | | | |

Note: All depths referenced to ground surface.

**FLOW TEST**

| Time (min) | Gauge Pressure (psi) (Hp) | Pressure Head (ft) (psi x 2.31) | Differential Head (ft) (Hg) | Calc. Total Head (ft) (H) | Water Meter ($ft^3$) (gal) | Water Flow (gpm) (Q) |
|---|---|---|---|---|---|---|
| Start | | | | | | |
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| | | | | | | |
| Start | | | | | | |
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| | | | | | | |
| Start | | | | | | |
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| | | | | | | |

Calculation of Hydraulic Conductivity :

$$K = Cp\ (Q / H)$$

K = Hydraulic Conductivity (ft per year)
Q = Constant Rate of Flow (gpm)
H = Total Head (ft)
Cp = Packer Coefficient = _____

Notes:

# BOREHOLE GEOPHYSICAL TESTING SOP

# BOREHOLE GEOPHYSICAL TESTING
# STANDARD OPERATING PROCEDURE

Geophysical, or downhole logging, involves lowering sensing devices into a borehole to record physical parameters that may be interpreted as specific rock characteristics. These data can then be used by the Project Hydrogeologist to evaluate stratigraphy, fracture zones, etc. Four logging tools will be used during this investigation as discussed below. The basic system involves a generator-powered unit that controls the tool output, receives data detected by the tool, and records the data on a chart. The unit contains a synchronized winch that raises and lowers tools into the borehole in time with the advancing chart recorder. Thus, the resulting logs furnish continuous records of subsurface conditions which may be compared or correlated from one well to another. The charted log data will allow rapid field interpretation and comparison with pre-existing logs, permitting immediate identification of correlative zones for well screen depth selection.

Borehole geophysical logging will be completed with a Mount Sopris MGX II digital logger. The MGX II is a totally software-controlled unit complete with a motorized wireline cable winch to handle the downhole tools. The tools used for this project will consist of the following.

## Natural Gamma Logging

Rocks and sediments contain traces of naturally occurring radioactive materials that emit gamma rays. The natural gamma tool detects the rate of gamma ray emissions. An electrical signal that is proportional to the number of gamma rays counted per unit time is sent continuously uphole from the tool to the logging unit. The probe registers gamma ray emissions measured in counts per second (cps) using a scintillation detector. Natural gamma logs may be obtained through steel or PVC casing, permitting logging inside cased holes or wells, and are not dependent upon a fluid-filled borehole. The natural gamma logs are used primarily for lithologic and stratigraphic correlation.

## Caliper Logging

The caliper log is a mechanical device that continuously measures the diameter of a borehole with depth. It is a useful tool for identifying less consolidated formations that have produced larger

diameter borehole sections. It is also useful in identifying horizontal fractures; however, vertical fractures are generally not detected by the caliper.

Temperature and Fluid Resistivity Logging

Temperature and Fluid Resistivity logging are used in locating and tracking sections in the borehole where fluids enter or exit. Both techniques are combined in a single logging tool (Mount Sopris 2PAF-1000, measuring 14.9 inches long by 1.5-inches in diameter). The tool is run in uncased boreholes, either after the fluid has equilibrated to natural temperature conditions or while pumping near the top of the water column to induce flow into the borehole. If the borehole fluid has equilibrated to natural temperature, the tool is logged downhole to avoid fluid mixing induced by the probe itself. If water is being pumped from the borehole to induce flow, the tool is lowered to the bottom of the borehole first and pumping (using a two-inch diameter pump) is initiated near the top of the water column. The rate of pumping will be dependant upon the yield of the test interval, with the objective of limiting the amount of drawdown (logging can not be conducted above the water surface). Logging should commence approximately five to ten minutes after initiating the pumping and pumping should continue until the logging is complete.

# WATER FLUTe LINER SYSTEM INSTALLATION SOP

# WATER FLUTe LINER SYSTEM INSTALLATION STANDARD OPERATING PROCEUDRE

The Water FLUTe is an alternative to conventional PVC monitoring wells that allows for the collection of water level data and water quality samples for analysis from multiple locations within a single borehole. The FLUTe system allows for the monitoring of multiple discrete intervals within a single borehole while sealing the borehole between the intervals of interest.

Upon reaching the final depth of the borehole, a blank FLUTe liner will be installed in the borehole in accordance with the manufacturers instructions (See vendor literature enclosed as part of this SOP). The blank liner will seal the borehole while the Water FLUTe is constructed in accordance with specifications provided to the manufacturer. These specifications will be the number, depth, and length of the monitoring intervals desired at that drilling location, as selected based upon the packer testing and geophysical logging results. This information will be provided to the FLUTe manufacturer and a Water FLUTe will be constructed to those specifications.

The installation of the Water FLUTe will commence by first removing the blank liner. The interior of the blank liner will be pumped out as it is pulled from the borehole and the used liner will be disposed of properly. The Water FLUTe will then be inverted into the borehole in accordance with the manufacturer's instructions (See vendor literature enclosed as part of this SOP).

Installation and removal of a blank liner or Water FLUTe is completed in accordance with the same procedures as outlined in the Manufacturers documentation attached with this SOP.

*Flexible Liner Underground Technologies, Ltd. Co.*
*6 Easy St., Santa Fe, NM 87501*

# Brief Summary of the FLUTe Water Sampling Systems

# and

# Installation Procedures

*A Medley of Innovative Designs*
*Phone: 505-455-1300*
*Fax: 505-455-1400*
*e-mail: Ckmist@aol.com*
5/00

## Background

Flexible Liner Underground Technologies (FLUTe) has been installing everting borehole liners for many years. Most of those installations were in the vadose zone for multilevel soil gas sampling. More recently, the same sealing liner system has been adapted to the use of multilevel sampling beneath the water table. In several respects, the installation is much easier than vadose zone installations, because no pressure canister is required. Hereafter are described several versions of the multilevel sampling system as used in a variety of circumstances.

## A wide range of installations is possible *

A pressurized coated fabric liner is used below the water table to seal and support the borehole wall just as it is used for other installations. However, there is a wide variety of boreholes and well geometries. The installations are described in the order of increasing complexity as follows:

1. Into a stable hole drilled in alluvium or rock
2. Into a cased well.
3. Into a hole supported by a rigid temporary casing or other liner
4. Into a cone penetrometer hole
5. Into a hole while it is being purged.
6. Into a hole sealed and supported by a blank liner.

## The basic water sampling system is very simple.

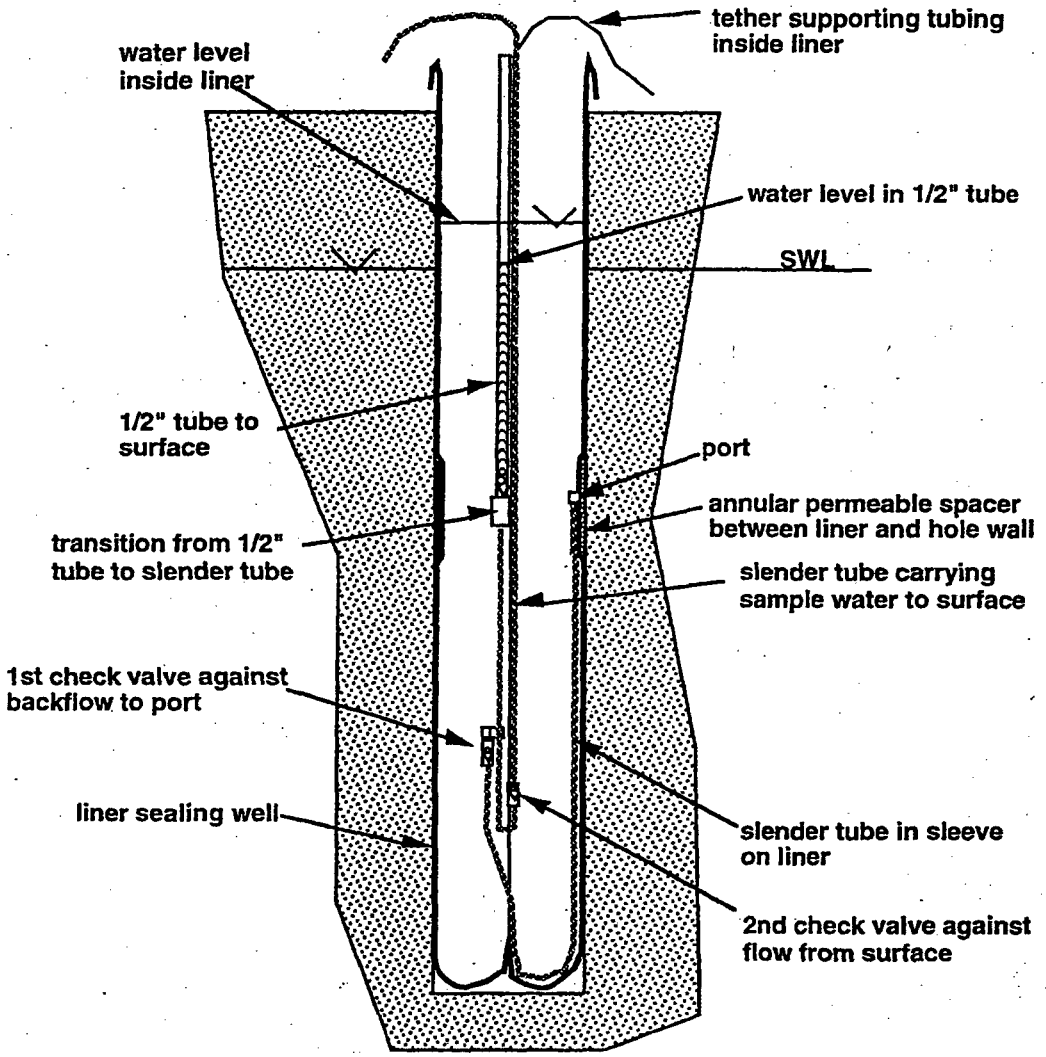
The sampling geometry is shown in Figure 1 (the *Water FLUTe*). The water filled liner supports and seals the hole. An excess head in the liner forces the liner against the hole wall. The sampling port draws water from the permeable annulus on the outside of the liner. The annulus draws water from the medium.

From the medium, the sample water flow is like that of a straddle packer. But unlike a straddle packer, there is no open hole above or below the sampled interval.

As the water flows into the port, it descends to the bottom of the hole in the tube (Fig. 1) and rises through the 1st check valve into the U shaped tube. The water rises into the large diameter side of the tube and equilibrates at the natural head level. The large tube diameter allows the water level to be tagged easily from the surface.

## Fig. 1. Slender hole valved tubing pumping system.

(only one port system shown for clarity)




The system is pumped by applying a gas pressure to the large tube. The water is driven downward through the bottom of the U and upward through the second check valve to the surface. This U tube geometry allows a large pump stroke and minimum effect of any sediment accumulation. The system can be driven by any of the several commercially available bladder or double valve pump driver systems.

The number of sampling ports is only limited by the number of U tubes that can be fit in the hole. Most of the hole volume is available for the tubing. Six sampling ports have been easily installed in a 3 in. hole. The pump lines can be connected to one air source and driven simultaneously

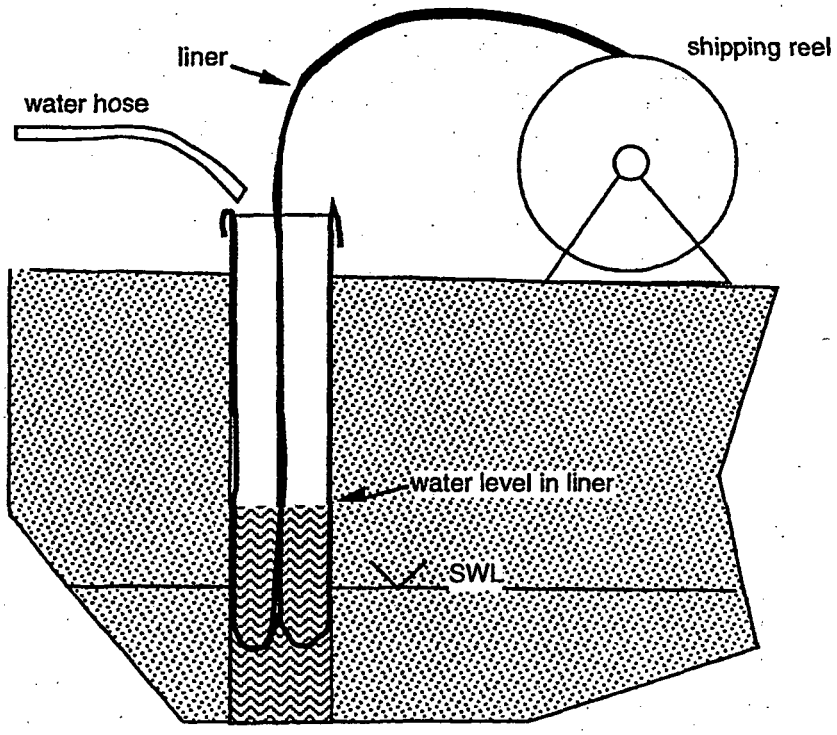
for rapid purging of the lines and sampling without introducing vertical gradients.

The system is highly reliable because of its simplicity and rugged construction. When filled with water, the system is easily and quickly removable by pulling up on the central tubing bundle to peel the liner out of the hole.

**Installation in a stable hole is very quick.**

The system is very easily installed in a stable or cased hole (Fig.2). The top of the liner is attached to the top of the casing or surface conductor. Water is added to the liner interior and it descends into the hole.

Fig. 2. Liner installation geometry




Typically, the liner and tubing bundle are fed into the hole from the shipping reel. The entire system can be emplaced in a hole in 5 minutes. Once in place, the wellhead is configured to support the tubing bundle.

The liner pressure can be maintained by an excess head of water in the hole or by filling the liner with a variety of materials including a cement grout or Bentonite slurry. The cement fill makes the well installation permanent.

**Installing in a cased well is very easy.**

Installation into a cased well with screens is just like that in a stable hole. In that case, the well is first installed with multiple screened levels in the usual manner. The sampling ports are located at each screen elevation. In some situations with very high medium permeability, the entire well has been screened to allow access to the medium. The liner is fit exactly to the casing size to seal the entire well against vertical flow.

The sampling liner can be quickly removed to allow other use of the well.

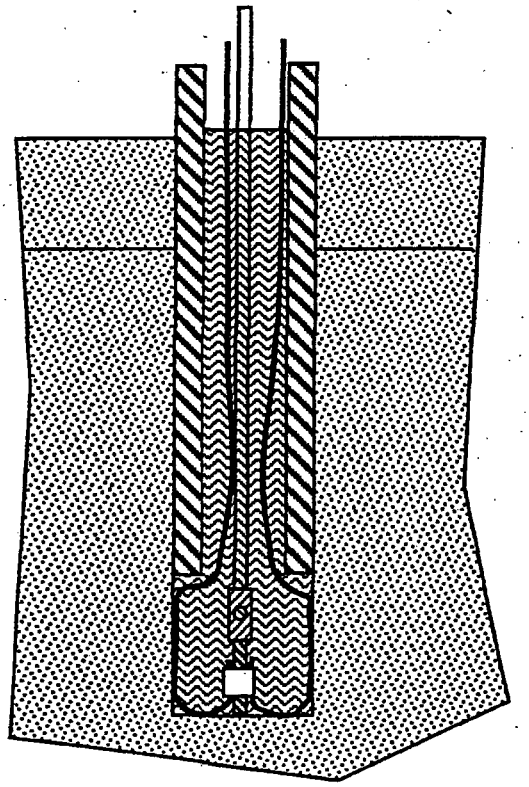
**Installation into a temporary casing or rigid liner avoids the unstable hole problem**

A technique has been developed to allow the installation of a flexible liner through the small interior hole of a cone penetrometer. The liner dilates to support the hole wall as the steel rod is withdrawn. The same technique allows the installation of the *Water FLUTe* system through the interior of other larger temporary casings. Examples of temporary rigid liners are driven casing drilling methods, sonic casing, or, pipe lowered into mud filled holes.

The installation is effected by lowering the FLUTe liner into the temporary casing (typically water filled), and lifting the casing as the liner dilates in the hole (Fig.3). The liner dilates in the hole to support the hole wall, but the liner does not dilate in the rigid casing. That is the essence of the FLUTe "trick" of installing through temporary casing.

A technique for installing the liner alone through a cone penetrometer has recently been tested in Nebraska and in Maryland (via a Geoprobe). After the rod is withdrawn, the multilevel water sampling system is installed inside the liner. This system is called a *Mini FLUTe* (The pumping geometry is not the U shaped tube.) Call for details.

Figure 3. Installation of a flexible liner through a casing



**The liner system has been installed into a hole while the hole is being purged from the bottom end.**

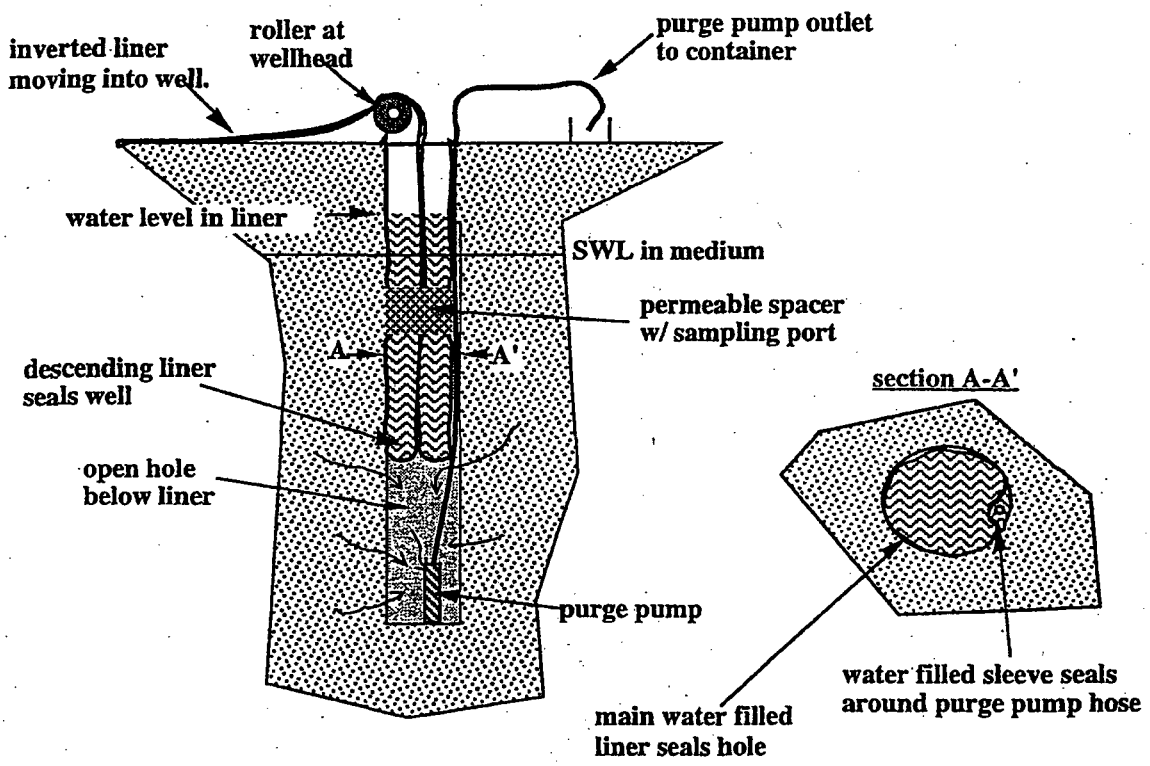
Since the everting liner descends like a piston to seal the hole, a purge pump can be emplaced at the bottom of the hole to pump the hole and surrounding medium as the liner descends to seal the hole. A technique has been devised to seal the purge pump lines against vertical leakage and to allow the purge pump to be removed after the liner is in place. The solution, of course, uses an everting liner. Figure 4 shows that geometry.

## Conclusion

FLUTe has adapted the flexible liner borehole seal and support technique to include a wide variety of simple, cost effective water sampling designs. Each design has the advantage of the continuous sealing liner, good sampling flows, high reliability, and easy removal. The use in Karst formations is especially advantageous. The technique has been used in a

variety of Super Fund situations with EPA approval. References are available from satisfied users. **For more information, call toll free: 888-333-2433 or e mail: ckmist@aol.com.** Our web site describes other FLUTe techniques: **www.flut.com.**

Fig. 4. Installation of liner while purging well/formation




*Note, all the flexible liner methods described herein are covered by FLUTe patents or patents pending.

# The *Water FLUTe* multi-level water sampling system

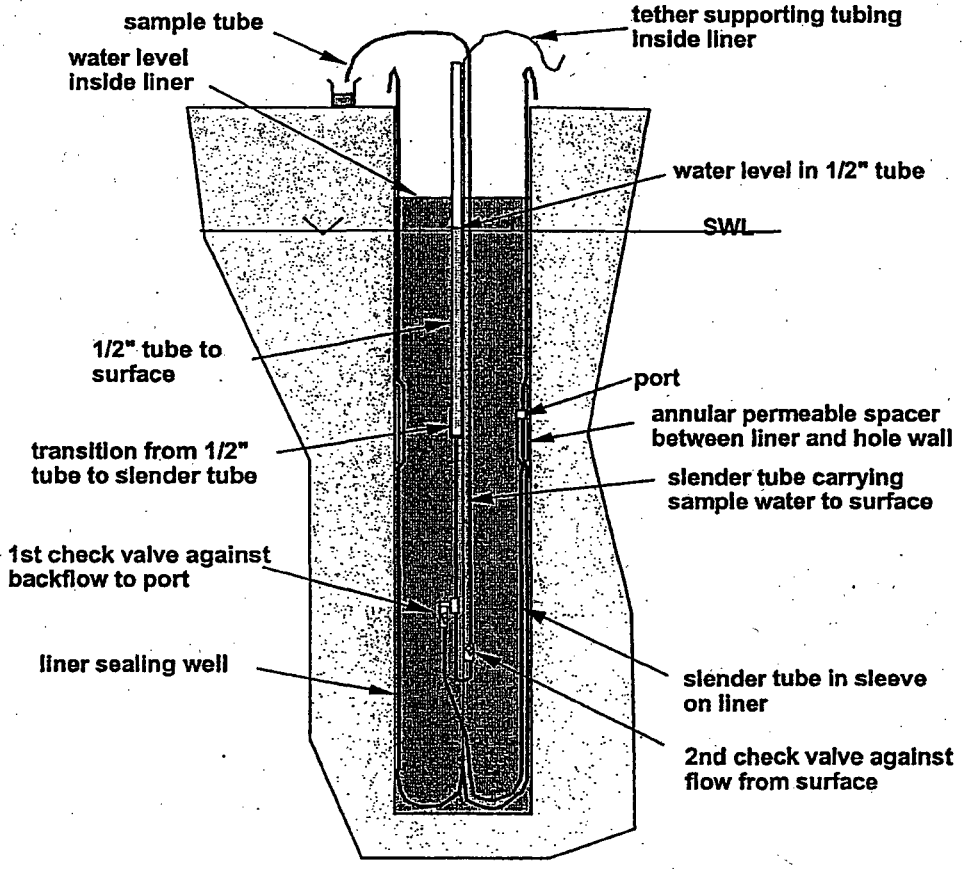
**Attributes:**

- Very compact. (often air freight)
- Easy to install ( some liners as quickly as 10 min. from setup, Milford, NH)
- Seals the entire hole against flow
- Draws sample directly from the formation
- Produces very small purge volumes
- Easy to purge & sample (20 min./5 ports)
- Allows individual head measurements for each port
- Allows many ports in one hole (5 to 30+)
- Is easily removed

**In place geometry:**

The installed geometry is shown for a single port. The dedicated tubing system is repeated for each port. The resulting tubing bundle is sheathed and occupies the interior of the liner.

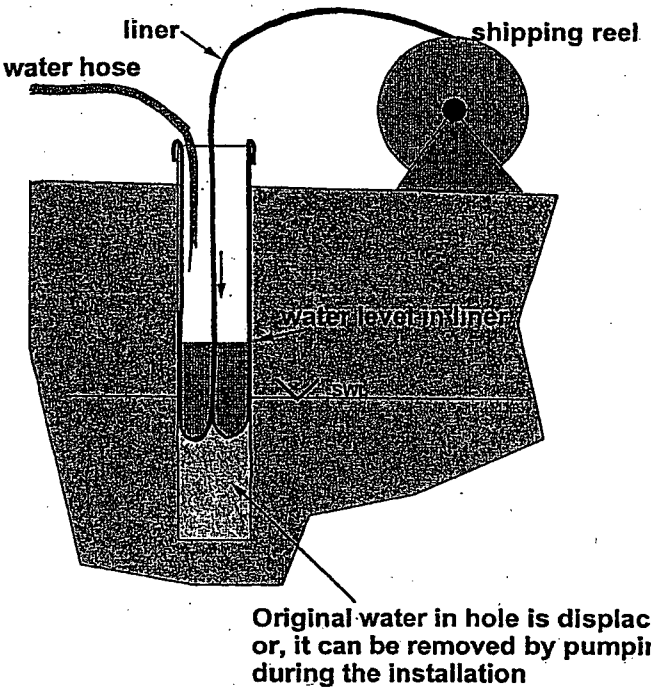
**(only one port system shown for clarity)**



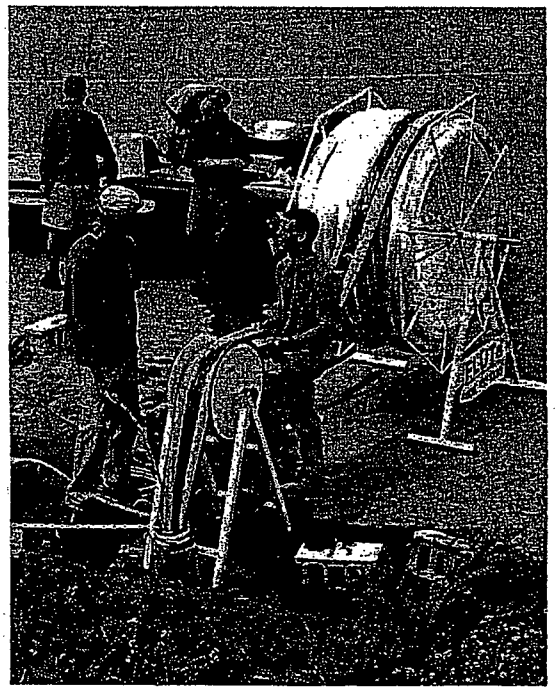

Flexible Liner Underground Technologies, Santa Fe, NM, 87501, ph 505-455-1300, web site: www.flut.com.

**Installation procedure:**
The liner is shipped on a reel, inside out. The top of the liner is attached to the surface casing and the liner is pushed, by hand, a short distance into the casing. Then one simply adds water to the interior of the liner, and it descends to the water table. Thereafter, more water is added to the liner to drive it into the hole. The water below the descending liner can be pushed into the formation, or it can be pumped from the hole as the liner descends.

## Just Add Water




**A typical installation:**
This installation was done at Cambridge, Ontario, for the Univ. of Waterloo. It is not very hard. The hole was uncased to 330 ft. with sampling 15 ports.



Completed wellhead for 15 ports with 15 pressure transducers.


Flexible Liner Underground Technologies, Santa Fe, NM, 87501, ph 505-455-1300, web site: www.flut.com.

## How does a *Water FLUTe* pump the water?

The question is often asked, "How does the pump work?" Or, does the pumping system apply a negative pressure (partial vacuum) to the sample water so as to cause out-gassing of volatiles? The pumping system does not drop the pressure in the sample to less than atmospheric pressure. The sample is pumped by positive pressure displacement through a pair of check valves.

**The water flow path in the tubing**

Figure 1 shows the Water FLUTe pumping geometry. The sample water flows from the formation through the layer of spacer material into the port and down the tubing to the bottom of the hole. From there the water flows upward through the first check valve (a Teflon ball check valve without a spring) into the U tube. In the U tube, the water rises to fill the left (large diameter) part of the U tube to the natural head level for the water in the formation. Some of the water flows up through a weak spring loaded second check valve in the slender tube half of the U tube. Due to the spring, the water level in the slender tube is not as high as in the "left" part of the U tube.

The spacer is fabricated of layers of monofilament mesh to allow easy water flow. The outer surface of the spacer is a fine woven filter fabric that prevents coarse silt size particles, larger than about 200 microns, from flowing into the tubing system.

Once the U tube has filled, the water level in the large tube can be measured from the surface with a slender water level meter of the common kind. That water level is that of the head in the formation at the port elevation. The first check valve is constructed with a deliberate small leak rate to allow the head in the U tube to follow that of the formation, even if the formation head is falling.

**The pumping stroke**

The water is pumped from the large diameter (left) portion of the U tube, through the second check valve, up the slender half of the U tube to the surface by gas pressure. See Figure 2 for the flow during the pump stroke.

A gas pressure source is connected to the top end of the large (left) tube via a convenient fitting. The pressure of the source is adjusted first to that needed to force the gas through the bottom of the U tube and hence driving nearly all of the water out of the tube. Remaining droplets are well aerated.

The U tube is allowed to refill as in Fig. 1.

The gas pressure is then reduced, so as to not drive gas through the bottom of the U tube. The gas pressure is applied again to the large left tube, forcing the water up the right hand slender tube to the surface, through the second check valve. The first slender tube volume is discarded to avoid the aerated droplets left in the first purge stroke.

The water flowing from the sampling tube is now of good quality. However, it contains some of the water from the spacer and the port to check valve tubing. This second stroke can be discarded.

The gas pressure is dropped, and the system refills from the port again.

The gas pressure is applied to the large tube for the third time. The sample(s) can be collected from this flow at any time. The first flow is that drawn directly from the formation.

**Pump capacity**

Since the pump stroke is the volume of the 1/2" id tube below the water table, the pumped water volume is often 1-2 gallons per stroke per port. In deep wells, it can be much larger.

This pumping system can be used for large depths limited only by the pressure capacity of the tubing. Even in that case, the pump can be operated with a series of short strokes to avoid the need for a pressure much larger than that to lift the water from the water table. For shallow water table situations (less than 1000 ft.), the maximum depth of the sampling liner is not limited by the pumping capacity.

**Simultaneous purge and sampling.**

The Figures 1 and 2 show a single port system. Each additional port on a liner has its own tubing components. The several tube pumping systems are gathered in a tubing bundle supported on the tether. Each sample port system can be pumped by itself in the same manner as above. However, the several systems can be pumped simultaneously by connecting the gas pressure source to all of the large "left" tubes at once, via a manifold.

Now, when the pressure is applied, all sampling tubes flow together. Likewise, all port systems fill simultaneously when the pressure is dropped. This reduces the time to perform the sampling by a great deal. It also discourages the drawing of water from one port region into another nearby port. Hence the sampling ports are better isolated from one another. In this way, ports can be located very near to one another for extraordinary high spatial resolution.

In some installations, several FLUTe systems in several nearby holes have all been pumped at one time. In that way, 6 ports in 6 wells were pumped simultaneously for 36 flowing sampling tubes at once. This was done for high temporal and spatial resolution.

Please address any questions about this *Water FLUTe* system to:

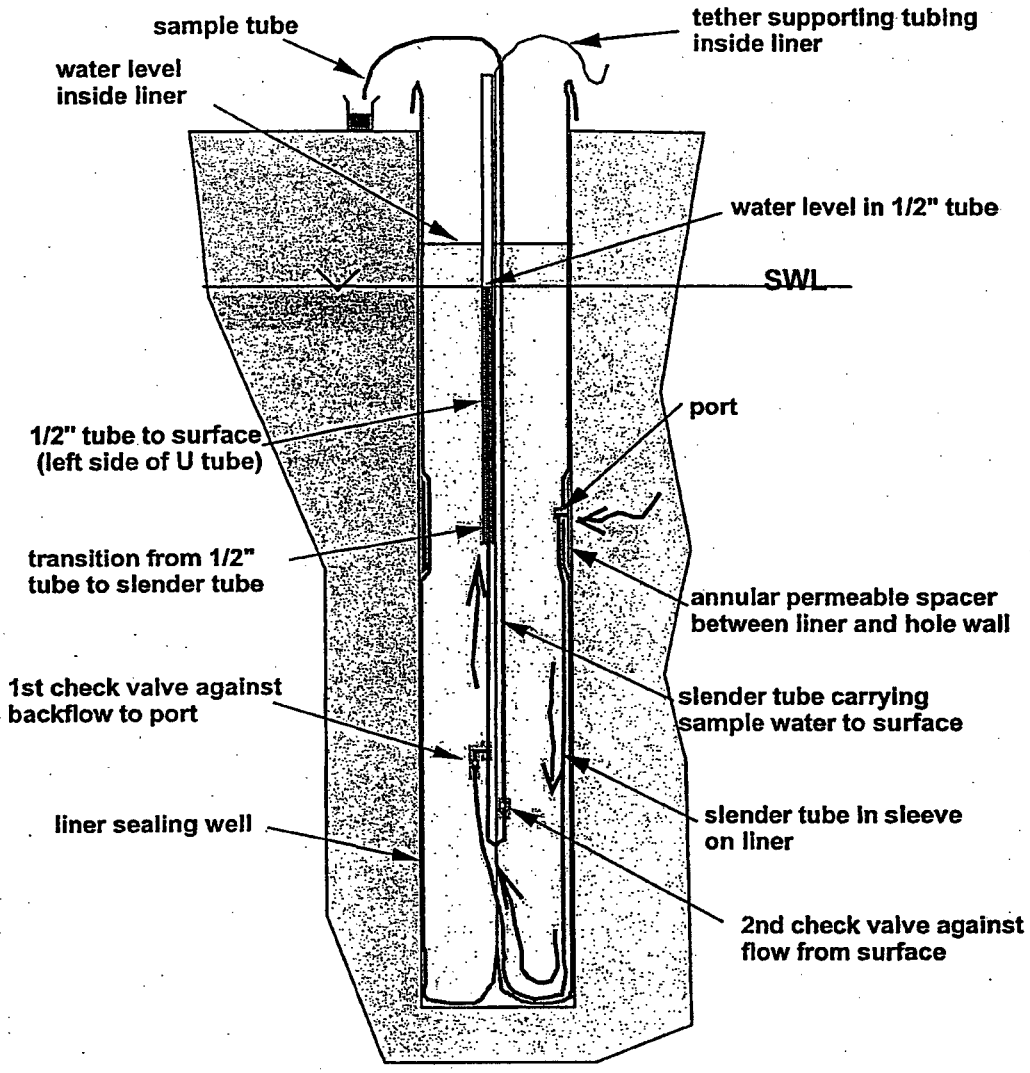
Flexible Liner Underground Technologies, Ltd. Co.
6 Easy St.
Santa Fe, NM 87501
888-333-2433
or, ckmist@aol.com

Custom designs for special situations are often provided.

It is noteworthy that the Water FLUTe system can be installed equally well in horizontally drilled holes. Systems can even be installed vertically upward with air pressure for collection of water samples from drill holes from underground tunnels.

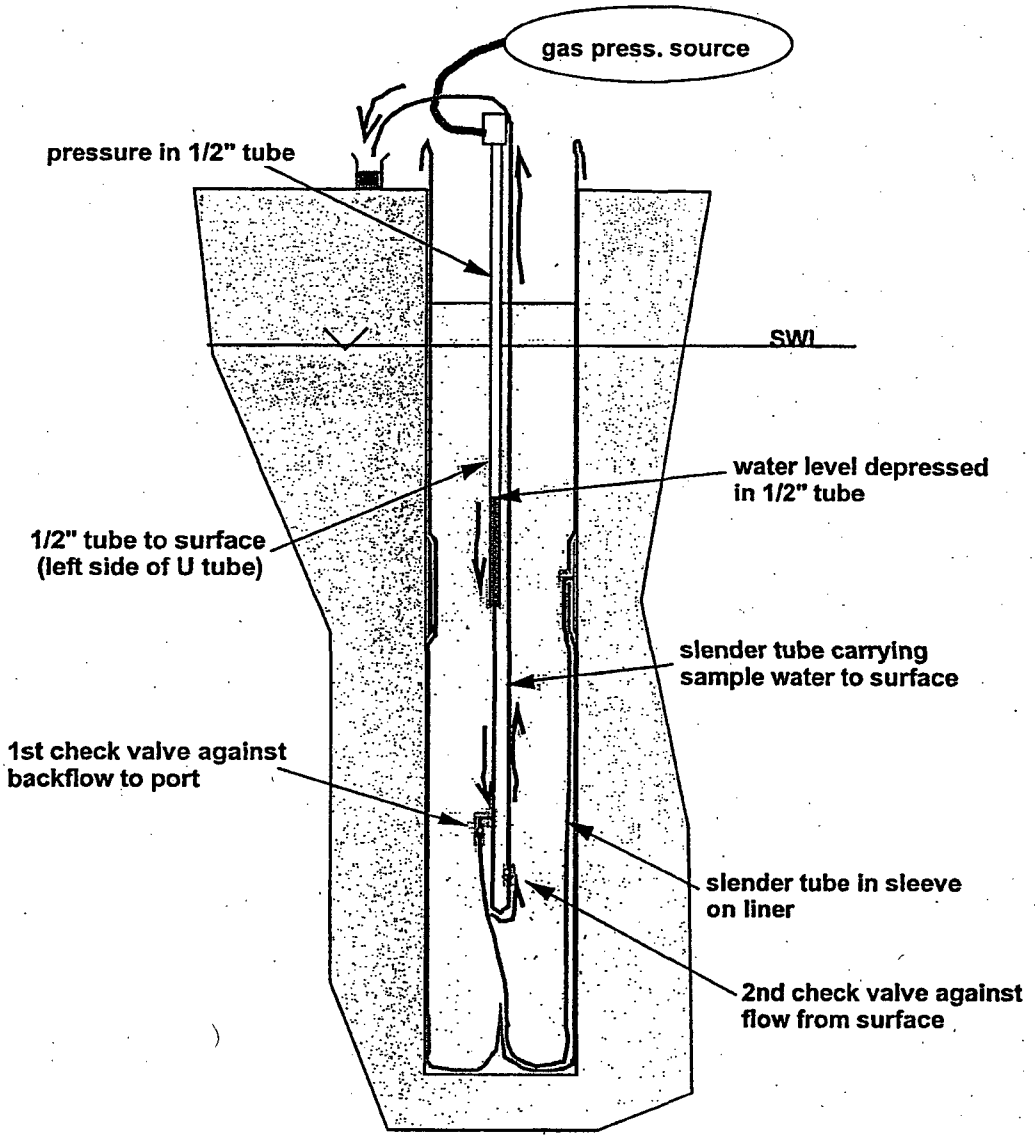
## *Fig.1. "Water FLUTe" valved tubing sampling system*

(only single port system shown for clarity)



## *Fig.2. Pumping stroke*

**(only single port system shown for clarity)**



*FLUTe*™ Flexible Liner Underground Technologies, Ltd. L.C.
For a medley of innovative designs
6 Easy St., Santa Fe, NM 87504
505-455-1300, www.flut.com

# Sampling guidelines for *Water FLUTe* systems

(valve tubing pumping system) rev. 2/23/04

## Water flow

Water flows from the formation into the spacer pore space, into the port, and fills the tubing. The first tube filled is the "port tube" volume that flows into the U tube. The U tube consists of the "large tube volume" and the "sampling tube volume" (see the attached drawing).

## Purging

Water is pumped from the tubing by applying a gas pressure to the interface at the static water level in the large tube. The water is driven down in the large tube and up through the second check valve to the surface via the sampling tube. By driving the water with a sufficient gas pressure to drive all of the water in the large tube and the sampling tube to the surface (the "recommended purge pressure"), the water in the U tube is nearly all expelled. The purge stroke is complete when gas is expelled following the water flow. The pressure in the system must then be vented, to allow the U tube to refill by flow via the port tube. The flow from the port tube consists of the port tube water, the water in the pore space of the spacer, and water from the medium. Because of the relatively large volume in the large tube, most of the recharge is from the medium. The recharge will take about as long as the first purge stroke. However, a tight medium will require more time.

Purging the U tube a second time will remove any of the water that has resided in the spacer and port tube volume. That is highly recommended, since the water resident in the tubing and spacer is probably not typical of the formation water. If the refill has been prompt, the second purge water volume will be similar to the first stroke. If in doubt, or if in a sedimentary formation or screened well, a third purge stroke is recommended to remove water that may have been in long contact with the liner or spacer.

## Sampling

The sampling flow is best driven on the third (or fourth) cycle by a pressure less than that needed to drive air through the bottom of the U tube. The pressure recommended is that which will drive the water to near, but not out of, the bottom of the large tube. That recommended pressure, "the sampling pressure," is calculated in the spreadsheet provided with each system.

*The first flow of the sampling cycle sweeps along droplets of water left in the tubing from the purge cycle. That residual water is depleted of volatile components. Tests have shown that the first tube volume of the sample flow should be discarded as depleted in volatiles (the sample tube volume is also calculated in the spreadsheet). Thereafter, the samples can be collected from the tube outflow. The volume to be discarded is shown in the spreadsheet as "wetted vol. sam. tube". The sample water flow rate will slow and finally stop. That occurs as the water column being driven approaches the applied pressure. The typical sampling pressure drives to within 20 ft. of the bottom of the pump tube (the U).*

This procedure should provide an ample sample of good quality drawn directly from the formation.

**Caution:** If the pumping system refills very slowly, there may not be sufficient water in the pump to fill the "sample tube" to the surface when the stroke is performed. In that case, there will be spitting of gas from the sample water and it will be followed by a flow of gas only. The sample water should never show "spitting" and the stroke should never end with gas flow from the sample tube. The proper sample flow will slow until it stops flowing. Should this evidence of insufficient recharge be observed, allow the pump to refill for a longer time. One can tag the water level in the large tube, as described in the head measurement procedure, to assure that the pumping system has been sufficient refilled.

**Measuring the head in the system**

The water level in the large tubes may not be the current water level. After sampling, if there is any leakage of the second check valve (sand in the tube, etc...) the water in the sample tube can backflow into the larger tube, adding to the water that fills the large tube during the recharge. Also, if the water level in the formation is dropping between head measurements, the water level in the large tube will not follow the descent if the first check valve is a good seal. For these two reasons, and for the freezing concern below, it is

best to finish the sampling stroke by raising the pressure to the purge pressure value to purge the pumping system of all water. Then upon refilling, the level is the current head for each port. If head measurements are made between sampling events, each port's pumping system should be first be purged to allow the tubing to refill to the current head value.

Note, an access tube is provided for tagging the water level in the interior of the liner. The liner water level should be maintained at the proper level (typically 10 ft above the water table, except for more shallow water tables) to assure that the liner is providing a good seal. If the level is less than that desired, add a small amount of water to raise the level. Be aware that for deep water tables, it may take up to 5 minutes for the water level to equilibrate after an addition. Do not overfill the liner. Estimate the correct addition based upon the hole diameter.

**If the water might freeze in the sampling tubing near the surface,** purge the entire volume of water from each sampling line, after sampling, before leaving it. Use the recommended purge pressure to remove all water, not the sampling pressure. **Each line should be blowing air/N2 when the purge is complete.** If the lines were purged after sampling for head measurements, that is sufficient.

**If the Water FLUTe uses PVDF tubing,** the purge of the entire system after sampling should not be neglected, even if head measurements are not to be made. This removes the water column in the sampling tube. For deep water tables, the long term pressure of the standing water in the sampling tube might lead to excessive creep of the tubing which is susceptible to "cold flow", a characteristic of Teflon like materials. (This is not a concern except for very deep water tables (>300 ft).

In most cases, the performance of a final purge of the system after sampling is useful, even if not essential.

**Simultaneous purge and sampling of all tubes**

The FLUTe pumping system for each port is essentially identical in length, pump volume and elevation in the hole. This allows all ports to be purged and sampled simultaneously for a great saving in sampling time. The only difference for simultaneous sampling is that the pressure source must

include a tube to each port fitting at the wellhead. The recommended purge and sample pressures are the same as used for single port sampling.

In some cases, the buoyancy of the sampling system is so great when emptied of water during the simultaneous purge that the tubing bundle can cause the liner to invert. The sampling volume spreadsheet provided with the liner notes whether the system can be purged simultaneously. This is only a problem for smaller hole diameters, many ports, and a small excess head in the liner. However, increasing the excess head in the liner to overcome the buoyancy of the tubing can be a hazard to the liner.

**A short summary is provided as the following checklist:**

Check List

1. Connect the gas driver source to the gas drive tube on the large tube. Set the regulator to the recommended purge pressure.
2. Expel the tube water at the suggested purge pressure. Collect the purged water volume for verification of a good purge. Note the water flow time of the purge stroke.
3. Allow the tubing to refill. Repeat the purge. Collect the purge volume to assure the amount removed is at least the "port tube volume". Was the refill long enough?
4. Purge a third time, if desired.
5. Allow the tubing to refill for the sample stroke.
6. Reduce the driving pressure to the "sampling pressure". Apply the pressure and collect the first flow to measure the discard volume. Discard that water.
7. Reduce the pressure, if needed, to slow the flow and collect the samples.
8. Perform a final purge of the water out of the sampling lines by raising the driving pressure to the purge pressure value.
9. When the sampling system has refilled, tag the water level, if desired, for the current water table. If a port system is refilling very slowly, tag it at a later time.

See the spreadsheet provided with each *Water FLUTe* for the recommended purge and sampling pressures. Those are the pressures that can be used for

a simultaneous purge of the several ports, but be sure that the buoyancy of the tubing will not lift the tubing, and the wellhead. The spreadsheet flags the condition where all ports should not be purged simultaneously. In most cases, several of the ports can be purged simultaneously.

**Optimum sampling procedure:**
Since it is often desirable to minimize the amount of time that the sample water resides in the pumping tubing, it is useful to note the actual time that is required for the recharge of the system. Since the fill rate slows dramatically for the last portion of the recharge, it is not necessary to wait for a complete refill. For most formations, the recharge is dominated by the tubing pressure drop. In that case, the time required for the purge stroke to be completed is about the same time required for the refill. (The exception is for a tight formation that recharges the tubing very slowly.) Hence the second purge can be started after waiting the same length of time as the first purge endured. If the second purge is of a similar volume (usually somewhat less) than the first purge volume, the refill time was long enough. After the same delay, the sampling stroke can be initiated. This timing of the strokes allows one to reduce the retention time in the pumping system. For very large sample volumes produced, the refill time can be shortened even more, as long as the sample volume is adequate after the discard of the first flow.

In some situations, the retention time is still too long. FLUTe can often increase the sample tube and port tube diameters for greater flow rates. However, the standard design is well matched for to a wide range of hole diameters, depths, and water table elevations. For very deep wells, the tubing may need to be of higher pressure capacity for the required driving pressures. For water table depths below 700 ft., this may be a concern. In some situations, the use of more expensive fluoropolymer (e.g. PVDF) tubing is warranted to minimize interaction with very low levels of contamination. The normal FLUTe tubing used until June, 2002 was Nylon 11 for its qualities of strength, relatively low contaminant absorption(compared to polyethylene), cost, and elasticity. Nylon 11 does leach butyl benzene sulphonamide in ppb levels. This does not interfere with most contaminant evaluations, in particular the chlorinated solvents and volatile organics. It can be mistaken for HE contamination if not measured carefully. FLUTe initiated a design change to all PVDF tubing in the Water FLUTe systems in 2002 to avoid any concern about tubing interaction with

the sample water. However, the prescribed purge is sufficient for the use of Nylon tubing systems.

**Questions:** Call 888-333-2433 and ask for Carl Keller, or a field engineer.

# Geometry of sampling system for each port

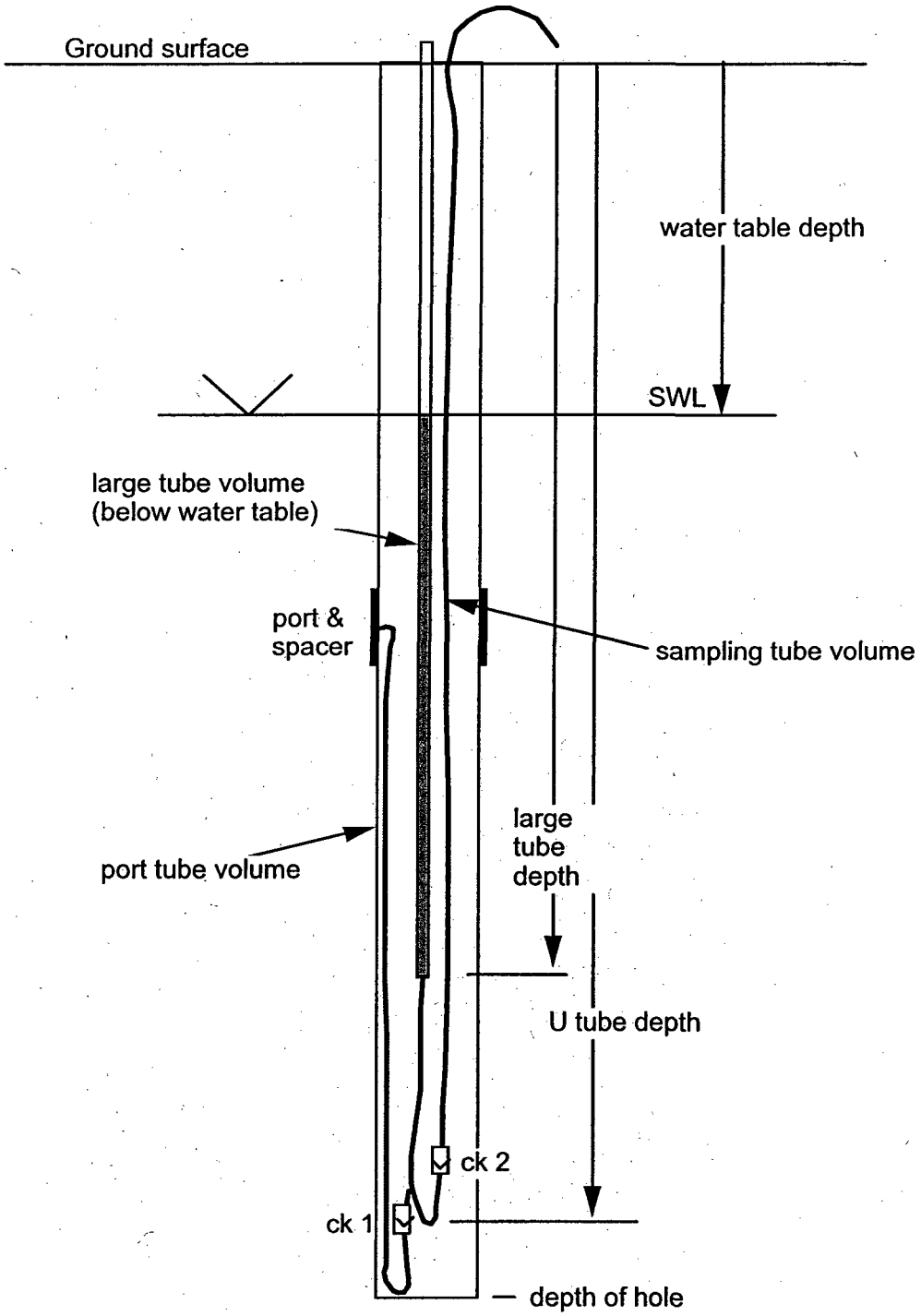
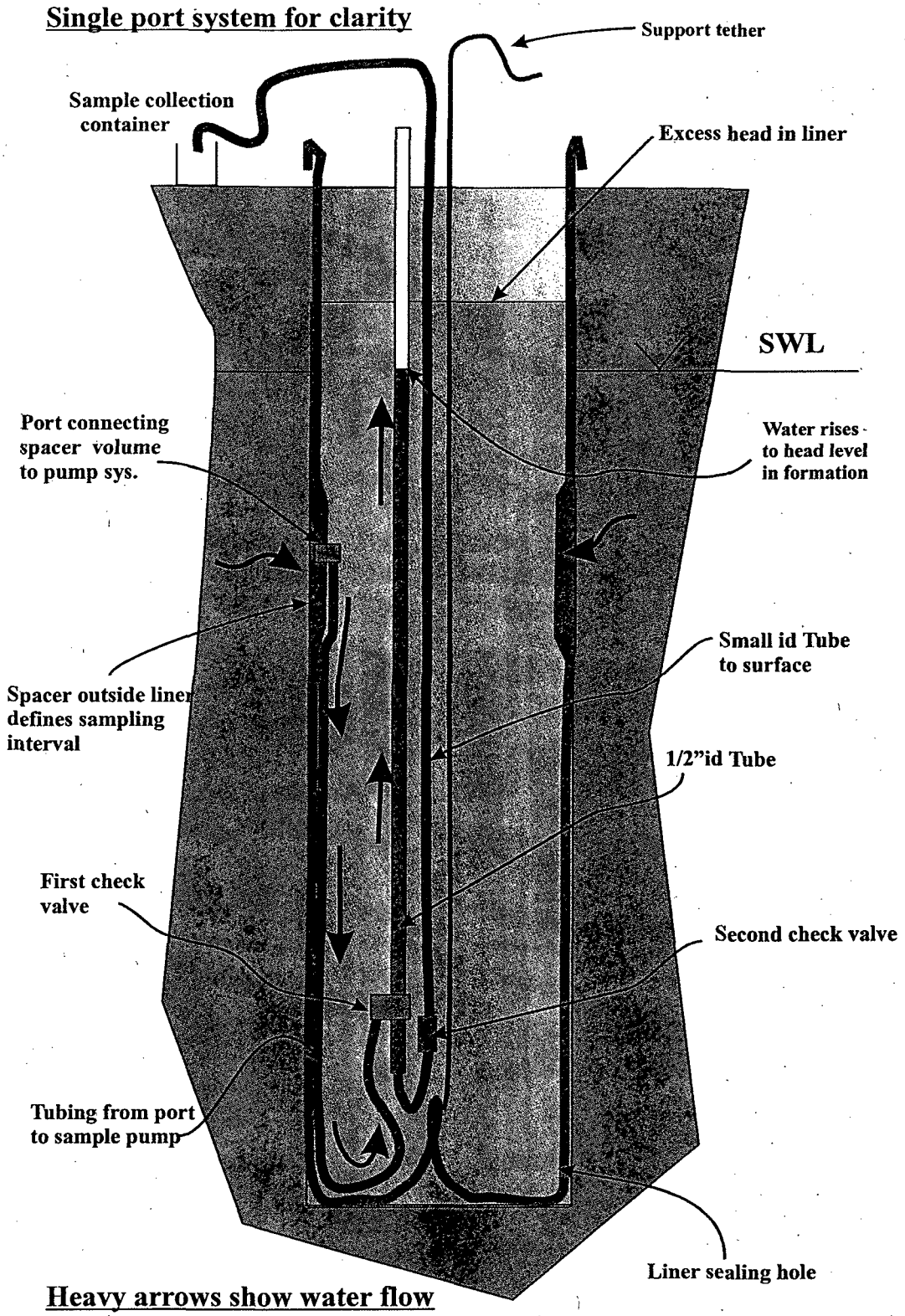
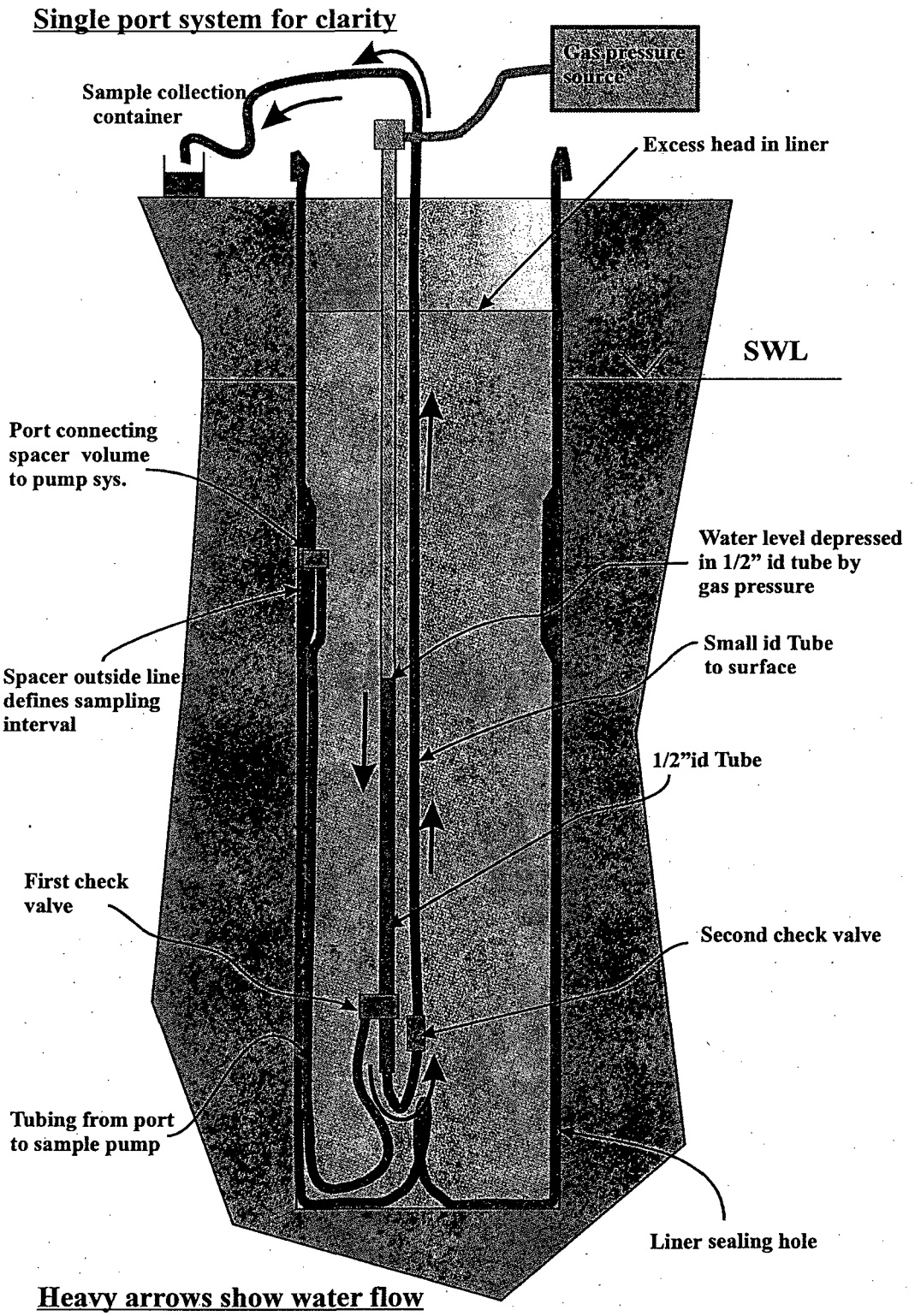


Fig. 1.. Water FLUTe valved tubing pumping system
(Recharge flow)



## Fig. 2. Water FLUTe Pump Stroke



# EQUIPMENT DECONTAMINATION SOP

# DECONTAMINATION
# STANDARD OPERATING PROCEDURE

An important aspect of quality control is the decontamination of field equipment. Improperly cleaned equipment can lead to cross-contamination and misinterpretation of data. The decontamination procedures used in this project are outlined in the following paragraphs.

## Decontamination Pad

The following activities and procedures will be used to contain and control liquids and solids generated from the decontamination of heavy equipment.

- An on-site decontamination facility will be constructed for use during the investigation. Water from the decontamination facility will be contained for proper disposal.

- The facility will be used for decontamination of drill rigs, drill rods and tools.

- In residential areas off-site, preliminary decontamination will be performed prior to traveling to the decontamination facility on-site. This will involve the removal and collection of loose solids that could potentially fall-off during transit. Removal of loose solids will be accomplished with a wire brush (or equivalent) without adding water.

- The equipment will be decontaminated by using water from a high pressure, hot water washer.

- Settled solids in the bottom of the sump will be treated in a similar fashion as drill cuttings. They will be shoveled into the appropriate containers for future disposal.

## Heavy Equipment

Drill rigs, drill rods, drill bits, and associated hand tools will be decontaminated at the site before drilling begins and between drilling locations. The equipment will be cleaned of mud, dirt, grease, etc., with a high-pressure hot water, jet spray.

### Water Level Indicators, Interface Probes, and Geophysical Probes

Upon completion of the liquid measurements, the probe will be raised to the surface and along with the wetted portion of the tape, will be decontaminated with the following procedure:

- Wash in potable water and non-phosphate detergent
- Rinse with potable water
- Rinse with deionized water

For wells that are located at or beyond the downgradient margin of the plume and which are expected to contain relatively low concentrations of dissolved contaminants, only the last two steps will be performed.

### Submersible and Bladder Pumps

When a submersible or bladder pump is used for well purging and/or sampling, it will be cleaned prior to and between each use. (Pump tubing will be discarded after each use.) The cleaning process will consist of the following:

- Flush a non-phosphate detergent solution through the pump by placing the pump in a bucket filled with the detergent solution.
- Flush potable water through the pump by placing the pump in a bucket filled with potable water.
- Rinse the internal and external portions of the pump with deionized water.

The power leads to the pump will be decontaminated in a similar fashion.

### Other Sampling Equipment

Other non-dedicated equipment used for the collection of samples to be subjected to chemical analysis will be decontaminated. This may include sediment sampling tools, stainless steel coring equipment, etc. which will be cleaned between each use by the following procedure.

- The equipment will be decontaminated using a non-phosphate detergent wash and potable water rinse between samples.
- 10% nitric acid rinse if sampling for metals

- Rinse with deionized water
- Acetone rinse (pesticide grade) if sampling for organics
- Rinse with deionized water
- Air dry
- Wrap in foil unless used immediately.

# ROCK CORE COLLECTION FOR LABORATORY TESTING SOP

# PROTOCOL FOR COLLECTING AND ANALYZING ROCK CORE SAMPLES FOR VOLATILE ORGANIC CHEMICAL CONCENTRATIONS AND PHYSICAL PROPERTY MEASUREMENTS

**Prepared by Beth L. Parker, Ph.D.**
**University of Waterloo**

**December 2005**

## TABLE OF CONTENTS



## LIST OF TABLES

# 1 Introduction

Rock coring and analysis is proposed to assess the potential effect on groundwater remediation of chemical diffusion of CVOCs [chlorinated volatile organic compounds] out of the rock matrix. This program will include the collection of rock core samples for determination of CVOC concentrations in the rock, apparent diffusion coefficient, total porosity, organic carbon content, pore size distribution, and hydraulic conductivity.

Dr. Beth Parker of the University of Waterloo [UW] has extensive experience in the evaluation of matrix diffusion phenomena. She will supervise the field and laboratory activities described in this SOP and will assist in evaluating matrix diffusion processes.

The purpose of this document is to describe the methods to be employed for measuring CVOCs such as tetrachloroethene (PCE) and trichloroethene (TCE) in the rock matrix. The protocols described here were prepared from a literature search for information on such methods used by others, and from previous studies conducted by the University of Waterloo (e.g. Parker and Sterling, 1999; Sterling, 1999; Sterling et al., 2005) at several sites where chlorinated solvent contamination is present within sedimentary rock environments.

## TECHNICAL APPROACH

Samples will be chosen close to fractures and fracture zones. Some samples will be selected also from between fractures. Approximately 4 rock core samples will be collected for the determination of apparent diffusion coefficients, total porosity, organic carbon content, pore size distribution and hydraulic conductivity of the rock matrix.

# 2 Field Methods

Matrix pore water chemistry and supporting measurements will be performed from continuous HQ cores collected from the top of rock to the total depth of the boring. An on-site geologist from HydroQual will be responsible for overseeing the drillers and preparing a daily log of drill site activities including a complete geologic log of the rock core that includes geologic descriptions, percent recoveries and RQD values for each core run, and notes from drillers regarding rate of drilling, gaps or notable losses or gains of drilling fluid. An on-site hydrogeologist and support technicians from the University of Waterloo will be responsible for the implementation of the rock core sample collection and analysis plan. Rock samples for CVOC analysis will be selected at locations along the core based on evidence of fractures and/or any apparent matrix property changes. Samples collected for CVOC analyses will be crushed and preserved in methanol in the field. All CVOC rock core samples will be analyzed at the University of Waterloo by direct, on-column injection into a gas chromatograph equipped with an electron capture detector (described later in more detail). Split aliquots of the methanol extract from 5% of the rock core CVOC samples will be sent to a commercial, New Jersey certified laboratory for VOC analysis, using either EPA Methods 8260B or 8021B, for laboratory and method comparison purposes. Samples for porosity, diffusion coefficient, foc and matrix permeability will be preserved for potential future testing, if needed.

## 2.1 THE ROCK CRUSHER

The rock crusher uses the Enerpac™ system, which is a commercial hydraulic press that provides the crushing power necessary to break up the rock samples. The core sample is placed in a stainless steel crushing cell and crushed with a stainless steel piston head using pressures as high as 3000 psi. The crushed sample is then pushed from the cylinder directly into a 125 mL, wide-mouth jar filled with a known volume of HPLC grade methanol. The amount of air passing by the sample while being crushed is minimized as well as the time required to completely crush the rock fragments into the desired particle size. The weight of the sample added to the sample jar containing the known volume of methanol is determined in the field with a field balance. CVOC concentrations are determined on a total mass of CVOC per unit mass of wet rock sample (μg/g). These

concentrations can be converted to equivalent pore water concentrations by knowing the partitioning of the total mass between the aqueous and sorbed phases. For this calculation values for the following parameters are used: wet and dry bulk densities for the rock, matrix porosity and solid phase organic carbon content.

## 2.2 CORE RETRIEVAL, SUBSAMPLE COLLECTION, HANDLING, AND PRESERVATION

Core runs will be in five to ten foot lengths, and the diameter will be HQ-sized (2.5 in/6.35 cm). Immediately on arrival of the cores at ground surface, they will be removed from direct sunlight and windy conditions to minimize volatilization of organic contaminants then placed in aluminum foil-lined PVC trays ( lengths of 4 or 6-inch diameter PVC pipe split along their length), for wrapping in a continuous sheet of clean aluminum foil. Aluminum foil will be used to keep most of the core covered while the geologist and hydrogeologist are inspecting the core for selecting sample locations based on lithology/ mineralogy, presence of fractures, nature of weathering, and evidence for groundwater and/or DNAPL fluid flow. The hydrogeologist will flag/mark the sections of the core to be subsampled for CVOC analysis.

### 2.2.1 CVOC Samples

Subsamples (i.e. core segments approximately 2-inches long) for determining CVOC concentrations will be taken from the cores immediately to minimize chemical losses due to volatilization. The initial core logging will be performed to identify key features for subsampling purposes and sections of core will be quickly broken from the core using a chisel and hammer, and then wrapped in aluminum foil for VOC and moisture preservation. After these samples have been collected, the core will be logged in more detail for the full geologic description. Additional sample types will be selected and removed from the core to represent selected fracture characteristics, lithologies and depths. For future reference, wooden spacers will be placed in the core boxes where core sections have been removed. Each spacer will indicate the sample ID, length and depth of the removed section, the date, and the purpose for which the sample was removed (type

of measurement).

There are three criteria for VOC sample selection. First, VOC samples will be taken immediately adjacent to (sample includes fracture surface) and 6 to 12 inches away from identified fractures, both above and below these features. All breaks in core should be suspected as being fractures in-situ, however, emphasis will be made on features with additional lines of evidence for active fluid flow (i.e. secondary mineral coatings/staining, slickensides, report from drillers regarding fluid loss/gain at specific depths during coring). These samples are intended for measuring the extent of diffusion into the matrix blocks away from fractures that may have once contained DNAPL phase or solute and the likelihood of DNAPL persistence at the time sampling. Second, additional CVOC subsamples should be collected where there is a distinct change in lithology /mineralogy that is not represented within the regular sampling interval. Samples will be collected from both sides of such boundaries, referred to as lithology pairs so that representative samples are collected from the different matrix materials. Third, duplicate samples will be collected at a frequency of 1/20. These subsamples will be taken from the same length of core split lengthwise (along the core axis) to provide samples along the same depth interval, thus ensuring the same lithology and analyte concentrations in both samples. After CVOC samples have been collected, a photograph of the core should be taken that identifies the top/bottom and depth interval of the core run, core location and date. The on-site geologist then continues logging the details and the hydrogeologist selects the physical property samples.

### 2.2.2 Procedures for CVOC Subsampling

The description below is a step-by-step outline of the process of rock core sampling.

1. Lay core in an aluminum foil-lined split PVC tray.
2. Note top/bottom of core and depth interval, measure length, and quickly identify features (fractures, breaks, lithology/facies changes, evidence of fluid flow (i.e. secondary minerals, precipitates, slickensides, etc.) to select sample locations.
3. Cover with the aluminum foil to minimize volatilization and evaporation of pore water.

4. Break off a two-inch section of core using a rock hammer and chisel, inserting a wooden spacer that specifies the depth interval that was removed and the type of sample taken (measurement to be made and ID).
5. If a field duplicate is planned, the disc length should be doubled to four inches and split lengthwise along the core axis using the chisel to produce two samples of nearly equal size that cover the same depth interval.
6. Completely wrap each sample in a piece of clean aluminum foil with a sample ID to minimize volatilization losses, and place in a cooler containing ice prior to crushing.
7. Place sample in the clean, dry rock crusher and crush sample.
8. Empty crushed sample into sample jar containing a known volume (~15 ml) of Purge and Trap grade methanol, taking extreme care to avoid splashing of methanol out of the jar. These sample bottles and screw caps with septum have been previously labeled and weighed both before and after filling with methanol, and again, immediately prior to their use in the field. There should be a minimum of 15 g of rock in each sample jar.
9. Record sample information (including a description (i.e. lithology pair, duplicate), the sample depth, location relative to any nearby fractures, etc.)
10. Clean rock crusher components, rock hammer, and chisel using the four part decontamination procedure explained in section 2.4.
11. During sample collection, trip blanks (always in triplicate), equipment blanks and field duplicates will each be collected after every 20 samples (each QA/AC sample type representing 5% of total sample number).
12. Clean outside of sample bottle and record total weight. Wrap screw cap lid-bottle seam several revolutions with Teflon tape, place sample jar in plastic bag with seal and wrap completely with bubble wrap for shipping. Place in cooler with respective trip blanks (each cooler contains at least 3 trip blank bottles that remain with specific batches of samples throughout shipping, storage and analysis) and keep on ice.
13. Chain of custody (COC) forms will be filled out at the end of each day of sample collection and shipped with each cooler back to the University of Waterloo.

14. Upon receipt of samples at the University of Waterloo, the COC will be signed, each sample will be logged in, re-weighed and shaken on the orbital shaker for 15 minutes, and shaken once per week for every week prior to analysis. Trip and equipment blanks are removed from the coolers and analyzed within the 14 day holding time for VOC samples. Storage blanks are added to the coolers for determining possibilities for cross-contamination of samples during the extraction period if held more than 14 days. It is important that each batch of samples be handled as a unit including respective QA/QC samples (trip and storage blanks, duplicates and equipment blanks).

The sample jars are 40 ml clear glass sample bottles with Teflon-lined septa and screw caps. Each labeled sample container and lid will be weighed empty, and re-weighed once the Purge and Trap grade methanol has been added to accurately determine the weight and volume of methanol extract emplaced in the container before being sent to the field. Before its use in the field, each container will be re-weighed to verify the volume of methanol, and will be weighed again immediately after sample collection to record the exact weight of each rock sample. There should be a minimum of 15 g of rock in each sample jar. Sample bottles will be stored in a cooler with ice or refrigerator set to 4°C until they are shipped back to the University of Waterloo where they are stored in a cold room at 4C until analysis. After the appropriate extraction time, aliquots of methanol from the sample containers will be analyzed for CVOCs at the University of Waterloo. Split samples of the methanol aliquots will be taken on 5% of the samples for CVOC analysis at a commercial, EPA certified laboratory for inter-laboratory and method comparison.

## 2.3 DECONTAMINATION OF DRILLING AND SUBSAMPLING EQUIPMENT

Decontamination procedures are designed to remove all traces of contaminants from the equipment to prevent cross-contamination of samples. If visible staining is observed on the core barrel, it will be cleaned between core runs using a 55-gallon drum of clean water and pressure washers. The hammer and chisel will be wiped down with a clean cloth soaked in methanol, followed by a clean cloth soaked in distilled water, and dried before re-use. Only those parts of the rock crusher that came into contact with the

subsamples require cleaning. This includes three components: the crushing cell, the crushing cell insert, and the screw-off piston. The procedure for cleaning these components consists of four steps. First, the parts will be cleaned in a phosphate-free detergent wash to get rid of the obvious sediment. The second step is full immersion in a clean (tap) water rinse, followed by a methanol (wash grade) rinse using a squirt bottle to remove any traces of contaminants not removed previously. The final step is a rinse with distilled (organic free) water using a squirt bottle to remove all traces of the methanol. The tools are then dried using clean paper towels before being used again. The soap and water baths will be changed on a regular basis, and equipment blanks will be collected on every twentieth sample by rinsing a clean crushing cell with HPLC grade methanol and collected in a 40 mL VOC sample bottle to be submitted for analysis along with the rock core samples. All cleaning fluids will be collected and treated or disposed of in the proper manner by GSC.

## 2.4 FIELD QA/QC

One equipment blank, consisting of Purge and Trap grade methanol rinsed through the rock crusher, will be taken after every 20 samples. Trip blanks equaling 5% of the total sample number or at least three trip blanks per batch of samples being stored in a cooler or box will be brought and stored with the methanol-preserved crushed rock samples for later analysis at the University of Waterloo. A trip blank is Purge and Trap grade methanol contained in a 40 mL CVOC sample container, is shipped to and from the field, stored with the CVOC samples, and unopened until time for analysis of the methanol aliquot. Duplicate samples will be taken every 20 samples on core sections of double length split along core axis so that the samples are taken from the same depth interval. All QA/QC samples will be identified on the chain of custody forms and tracked throughout the sample handling and analysis process.

# 3 Laboratory Methods

The University of Waterloo will conduct the majority of the analyses. Duplicate analyses of the methanol extract will be performed on 5% of the rock CVOC samples and internal standards by a commercial, certified laboratory for method and laboratory comparison purposes.

## 3.1 SAMPLE ANALYSES METHODS

### 3.1.1 CVOC Sample Extraction

Methanol extraction is expected to remove the sorbed as well as the dissolved phase contaminants from the rock matrix and prevent loss of these volatile constituents from the sample container during the extraction time period required.

Each sample will be sonicated to facilitate the extraction of pore water into the methanol. Sound waves are used to mix the methanol and maximize the mixing of the matrix pore water and organic constituents into the extractant. Samples will be allowed to extract in a cooler/refrigerator at 4°C for a minimum of four weeks prior to performing the CVOC analyses. These time periods have been selected to minimize CVOC losses due to long holding times and are within the time periods typically used for extraction of volatile organic constituents from clay samples. To check the completeness of the extraction, ten percent of the CVOC samples will be analyzed two weeks following the initial analyses for comparison of the amount of mass measured in the same samples (replicate analyses with a time lag). Alternatively, research conducted at the University of Waterloo has shown that micro-wave assisted extraction of volatile organic contaminants such as TCE can accelerate extraction times. Regardless of extraction technique, time-series samples as mentioned above will be taken to confirm completeness of extraction.

### 3.1.2 Pore Water CVOC Concentrations

Previously, rock samples that were preserved in HPLC grade methanol were sent to a contract laboratory and analyzed using EPA method 8021B (US EPA, 1996). This provided a detection limit of 50 μg of TCE per litre of methanol. This protocol has been modified to provide improved detection limits using equipment and methods developed at the University of Waterloo for quantification of selected VOC compounds,

specifically, those listed in Table 2. However, five percent of the total number of samples that are analyzed at the University of Waterloo will also be sent to a commercial laboratory for laboratory cross-check purposes using EPA method, (8010/8021B/8260B). The commercial lab will screen for the complete list of VOC analytes (as listed in Table 1). Rock samples collected in the 125 ml glass sample jars will be sent to the University of Waterloo for analysis. After the CVOCs have been completely extracted into the methanol, an aliquot of methanol will be injected directly into a gas chromatograph (GC) for separation and quantification using a microelectron capture detector (μ–ECD). The list of analytes to be quantified is provided in Table 2.

The direct, on-column injection of methanol onto the gas chromatograph has been currently tailored for analysis of PCE, TCE and relevant breakdown products so that the resulting detection limit and run times are significantly lower than that reported by the previous contract laboratory (Table 2). These improved detection limits in methanol have been converted to equivalent pore water concentrations for those compounds studied in our method development. The GC specifications for the new methanol direct on-column injection technique are summarized below:

- GC: HP 6890 with autosampler
- Column: HP-1 30m, 0.32mm ID, 4μm stationary phase
- Injection: 1μL liquid, cold on-column
- Carrier gas: Helium
- Detector: μ–ECD
- Analysis turnaround time: 17 minutes

***Table 1. List of Analytes in EPA Method 8021B/8010 Analysis***

| Analyte | Preparation Method | Analysis Method | MRL (µg/mL of MeOH) | Minimum Detection Limit (µg/mL MeOH) | Maximum Detection Limit (µg/mL MeOH) |
|---|---|---|---|---|---|
| Dichlorodifluoromethane | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| Chloromethane | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| Vinyl Chloride | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| Bromomethane | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| Chloroethane | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| Trichlorofluoromethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,1-Dichloroethene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Methylene Chloride | EPA 5030 | 8010 | 0.2 | <0.2 | <2.0 |
| Trans-1,2-Dichloroethene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Cis-1,2-Dichloroethene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,1-Dichloroethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Chloroform | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,1,1-Trichloroethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Carbon Tetrachloride | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,2-Dichloroethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Trichloroethene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,2-Dichloropropane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Bromodichloromethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 2-Chloroethyl Vinyl Ether | EPA 5030 | 8010 | 0.5 | <0.5 | <5.0 |
| Trans1,3-Dichloropropane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Cis-1,3-Dichloropropene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,1,2-Trichloroethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Perchloroethene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Dibromochloromethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Chlorobenzene | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| Bromoform | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1,1,2,2-Tetrachloroethane | EPA 5030 | 8010 | 0.05 | <0.05 | <0.5 |
| 1.3-Dichlorobenzene | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| 1.4-Dichlorobenzene | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |
| 1,2-Dichlorobenzene | EPA 5030 | 8010 | 0.1 | <0.1 | <1.0 |

***Table 2. Comparison of Old and New Method Detection Limits (MDL)***

| Analyte | New Method MDL (µg/L): On-Column Injection (µg/L MeOH) | Old Method MDL (µg/L pentane) | Example New MDL Equivalent GW Conc. (µg/L)* |
|---|---|---|---|
| 1,1-Dichloroethene | 7.0 | 35.0 | 0.41 |
| t-1,2-Dichloroethene | 5.5 | 75.0 | 0.43 |
| c-1,2-Dichloroethene | 3.5 | 50.0 | 0.34 |
| Trichloroethene | 0.07 | 2.0 | 0.27 |
| Perchloroethene | 0.07 | 1.0 | 0.12 |

*Note: We bulk density=2.45 g/cm$^3$; matrix porosity=13%; R(11DCE)=2.1; R(TCE)=3.3; R(PCE)=7.6 and assuming 40 cm$^3$ of rock in 60 mL of MeOH.

## 3.2 LABORATORY QA/QC

A minimum of five percent of all methanol preserved subsamples will have aliquots of the methanol extract removed after the samples have been allowed to fully extract. These aliquots will be sent to an EPA certified laboratory for independent confirmation of analyte concentrations. Spiked methanol aliquots of known concentration will also be sent to the certified laboratory to compare the different analytical techniques. A minimum of five percent of all samples collected in the field will be split duplicates and will be analyzed by the University of Waterloo. Laboratory duplicates and blanks are also created and analyzed with each batch of samples at the rate of 5%.

# 4 PHYSICAL PROPERTY MEASUREMENTS ON CORE SAMPLES

## 4.1 Porosity Sample Collection

Samples will be selected from existing core stored on site and an effort will be made to obtain samples from different lithologies or where variations in lithology occur as assessed during the logging of the core.

Each sample will be a cylindrical disc of the same diameter as the HQ core (2.5 inches/6.35 cm) that is retrieved from the core barrel, with a height of approximately 2 to 6 inches. The sample will be collected using a hammer and chisel. The sample will be wrapped in plastic and taped with a label indicating the core location, depth interval, and date of coring and date of sample collection.

## 4.2 Chloride Diffusion Coefficient and Permeability Sample Collection

Samples will be selected from existing core stored on-site to represent the bedrock formation over the relevant depth interval. Six to twelve inch lengths of core (full diameter) will be selected, wrapped in aluminum foil and plastic wrap and taped with a label indicating the core location, depth interval, and date of coring and date of sample collection.

## 4.3 Fraction of Organic Carbon

Subsamples for fraction of organic carbon will be taken from the above samples as required. Care will be taken to ensure that these samples are distributed throughout the length of the cored zones in the corehole and are selected to represent the variations observed in the core. The solid phase organic carbon content is useful for estimating the sorbed fraction of CVOC constituents in the rock samples.

# 5 References

Gorecka, M. , T. Gorecki, and B. L. Parker, 2001, *Automated Cool On-Column Injection for Highly Sensitive Determination of Chlorinated Solvents in Soils and Rocks*. In: *24th International Symposium on Capillary Chromatography and Electrophoresis*, May 20-24, 2001, Las Vegas, NV.

Navon, D., K. J. Goldstein, A. R. Vitolins, B. Parker, J. A. Cherry, G. A. Anderson and S. P. Wood, 2004, *In Situ Chemical Oxidation Using Permanganate for Remediation of Chlorinated VOCs in Fractured Shale*. In: A. R. Gavaskar and A. S. C. Chen, Ed., *Remediation of Chlorinated and Recalcitrant Compounds – 2004, Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. May, 2004, Monterey, CA, Battelle Press, paper 2F-02.

Parker, B.L., J.A. Cherry and R.W. Gillham, 1994, *Diffusive disappearance of immiscible-phase organic liquids in fractured geologic media*. Ground Water, v. 32 (5), pp. 805-820.

Parker, B.L, J.A. Cherry and R.W. Gillham, 1996, *Effects of molecular diffusion on DNAPL behavior in fractured porous media*, Chapter in *Dense Chlorinated Solvents and Other DNAPLs in Groundwater*, eds. J.F. Pankow and J.A.Cherry, Waterloo Press, 522 pp.

Parker, B.L. and S.N. Sterling, 1999, *Rock core subsampling and analysis for volatile organic compounds in a fractured sandstone*. In Symposium Proceedings *Dynamics of Fluids in Fractured Rocks: Concepts and Recent Advances*, February 10-12,1999, Berkeley, CA. Abstracts pp. 175-177.

Parker, B. L., 2003, *Strong Matrix Diffusion Effects on Contaminant Behavior in Fractured Sedimentary Rocks*. Presented at: *Geological Society of America Annual Meeting*, November 2-5, 2003, Seattle, WA, Geological Society of America Abstracts with Programs, v. 35, no. 6, p. 372.

Parker, B. L., J. A. Cherry, K. J. Goldstein, A. R. Vitolins, D. Navon, G. A. Anderson and S. P. Wood, 2004, *Matrix Influence on Contaminant Mass Distribution in a Fractured Shale*. In: A. R. Gavaskar and A. S. C. Chen, Ed., *Remediation of Chlorinated and Recalcitrant Compounds – 2004, Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. May, 2004, Monterey, CA, Battelle Press, Abstract 1B-34.

Parker, B. L., 2004, *Utility of Rock Core for Characterizing Contamination in Fractured Sedimentary Rocks*. In: *Proceedings of the U.S. Environmental Protection Agency / National Ground Water Association Fractured Rock Conference: State of the Science and Measuring Success in Remediation*. September 13-15, 2004, Portland, ME, p. 370-371.

Sterling, S.N. 1999, *Comparison of Discrete Depth Sampling Using Rock Core and a Removable Multilevel System in a TCE Contaminated Fractured Sandstone*. M.Sc. Thesis, Department of Earth Sciences, University of Waterloo, 108 pp.

Sterling, S. N., B. L. Parker, J. A. Cherry, J. H. Williams, J. W. Lane Jr., and F. P. Haeni, 2005, *Vertical Cross Contamination of Trichloroethylene in a Borehole in Fractured Sandstone*. Ground Water, v. 43, (In Press).

U.S. Environmental Protection Agency (EPA), 1996, Test methods for evaluation solid waste, physical/chemical methods. *SW-846, Final Update III*, Revision 2. Method 8021B, Aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors.

Vitolins, A. R., K. J. Goldstein, D. Navon, G. A. Anderson, S. P. Wood, B. Parker, and J. A. Cherry, 2004, *Technical and Regulatory Challenges Resulting from VOC Matrix Diffusion in a Fractured Shale Bedrock aquifer*. In: *Proceedings of the U.S. Environmental Protection Agency / National Ground Water Association Fractured Rock Conference: State of the Science and Measuring Success in Remediation*. September 13-15, 2004, Portland, ME, p. 115-126.

# MONITORING WELL CONSTRUCTION SOP

# CONTENTS

# MONITORING WELL INSTALLATION STANDARD OPERATING PROCEDURE

The following SOP is consistent with requirements of NJDEP's Field Sampling Procedures Manual (August 2005), Appendix 6.1 Monitor Well Construction and Installation, and as provided in N.J.A.C. 7:9D-2.4. All wells must be installed by a New Jersey-licensed well driller of the appropriate class. Prior to installing a well, the well driller must obtain a well drilling permit from the Bureau of Water Allocation (BWA). Within 90 days of completing a well, the well driller must submit a well record to BWA.

## WELL DIAMETER

Wells shall be a minimum of 2 inches in diameter but may need to be larger to accommodate submersible pumps or other sampling and testing equipment. In all cases where wells are installed in oversize boreholes, the borehole diameter must be a minimum of four inches larger than the well casing diameter.

## WELL CONSTRUCTION MATERIALS

Overburden monitor wells should be constructed with either polyvinyl chloride (PVC) or stainless steel casing and screen. Stainless steel should be used in the presence of free product which may degrade the PVC. However, stainless steel should not be used in highly corrosive waters since metals may leach from the stainless steel causing detection of false positives in water samples analyzed for metals.

Bedrock wells are typically constructed using carbon steel casing with the intake of the well being an open hole in the bedrock. In cases where the bedrock is friable, well casing and screen may be installed in the borehole of a bedrock well. In this case, installation of an outer casing (double-cased well) may not be necessary, particularly in the case of shallow bedrock.

## SCREEN LENGTH

The maximum length of well screen (or open borehole in bedrock wells) for monitor wells is 25 feet. The purpose of this limitation is to minimize the potential to cross-contaminate uncontaminated

aquifers. In most cases, screen length should be minimized (e.g., 5 to 10 feet of screen) if sufficient well yield is available to allow sampling of the well. In cases where low-flow sampling is intended in newly installed monitor wells, the wells should be installed with no more than five feet of screen. In cases where a well will be used for groundwater recovery, injection, air sparging, soil vapor extraction or aquifer testing, construction of the well with more than 25 feet of screen or open borehole may be acceptable, with prior approval from NJDEP.

## SCREEN SLOT SIZE AND FILTER PACK MATERIALS

Filter pack material should be clean silica sand which is sized according to the texture of the borehole materials from sieve size analysis data. The uniformity coefficient of the filter pack materials should not exceed 2.5. The screen slot size should be selected to retain at least 90% of the filter pack material. No more than five feet of filter pack should be placed above the well screen. The top of the filter pack may be graded from coarser to finer (going upward) to minimize penetration of the overlying grout.

## GROUTING MATERIALS

The annular space in wells must be sealed to prevent the borehole from acting as a conduit for vertical migration of contamination. All grouting materials should be installed as a slurry using a side-discharge tremie pipe in order to prevent invasion of the grout into the filter pack. Examples of material include Portland cement, high-grad bentonite and Portland cement/high-grade bentonite mixtures. The installation of a bentonite seal above the filter pack using bentonite pellets is not permitted.

## WELL DEVELOPMENT

All well development or redevelopment work shall be performed by a licensed well drill of the proper class. The objective of a monitor well is to provide a representative sample of water as it exists in the formation. Therefore, well development must restore the area adjacent to the well to its indigenous condition by correcting damage done to the formation during the drilling process. Monitor well development is required to: remove drilling fluid residues remaining in the borehole or surrounding aquifer during the drilling procedure; restore the hydraulic properties of the formation immediately surrounding the monitor well, and; sort the filter pack material to allow ground water to freely flow to the monitor well.

Acceptable well development methods include: bailing, overpumping, mechanical surging, air-lift surging, and water jetting. The best methods involve surging water flow back and forth through the well screen to sort the filter pack materials. Following the use of these methods, the wells must be pumped to remove the fines from the wells. The use of chemicals to increase or restore the yield of monitor wells is not acceptable.

Well yields determined during the development of monitor wells and the well development method(s) used should be recorded on all well logs, well records and as-built construction diagrams. Well development should not be performed until a minimum of eight hours after the well has been installed, to allow time for the cement grout to set.

## SPECIFICATIONS FOR FLUSH MOUNT WELLS

In some circumstances (e.g., operating service station), it may be impractical to install wells with casing above the surface. In such situations, flush mounted wells may be installed. Flush mounted wells must be installed with road boxes specifically manufactured for wells. The road box must be of the type with bolt-down lids, waterproof and able to withstand vehicular traffic. The lid must be clearly labeled as a monitor well. The road box must be firmly anchored to, or embedded in, a concrete surface seal. The concrete seal must be sloped away from the box, providing drainage for water and easy vehicular traffic. The road box shall extend slightly above the surface (1-2 inches) to prevent pooling of water on the bolt-down lid.

By the nature of their design, flush-mounted well boxes cannot be locked from the outside. As such, flush-mounted well boxes must be completed with a lockable cap on the inner casing. This cap must be water-tight. No vent hole shall be drilled in the cap or casing. In addition, flush-mounted well boxes must be large enough to allow adequate room to install and remove the lock and cap from the inner casing. There must also be adequate room to secure the flush-mounted box lid with the inner cap locked in place (See Figure 1).

## MONITORING WELL SPECIFICATIONS FOR BEDROCK FORMATION

1. The construction of all monitoring wells shall be in accordance with the requirements of N.J.A.C. 7:9D-2.2 et seq.

2. The use of glues or solvents is prohibited in the installation of well screens, riser pipes and well casings.
3. The locking cap must be made of steel.
4. A New Jersey-licensed surveyor must survey top of the innermost casing (excluding cap) to the nearest 0.01 foot. The survey point shall be the highest point of the casing. If the casing is level, the survey point shall be established on the northern side of the casing. The survey point must be marked on each well via notching or indelible marker.
5. Details for a Bedrock Formation Well are shown on Figure 2.

## MONITORING WELL SPECIFICATIONS FOR UNCONSOLIDATED AQUIFERS

1. The construction of all monitoring wells shall be in accordance with the requirements of N.J.A.C. 7:9D-2.2 et seq.
2. Minimum screen and riser pipe inner diameter is 2 inches.
3. The use of glues or solvents is prohibited in the installation of well screens, riser pipes and well casing.
4. In order to prevent any induced interconnection between the overburden/weathered bedrock and competent bedrock, the well screen shall not extend across the aforementioned interface.
5. Wells must have a filter pack installed.
6. When grouting the annular space directly above a filter pack, the grout should be discharged horizontally from the tremie pipe.
7. The locking cap must be made of steel.
8. A New Jersey-licensed surveyor must survey top of the innermost casing (excluding cap) to the nearest 0.01 foot. The survey point shall be the highest point of the casing. If the casing is level, the survey point shall be established on the northern side of the casing. The survey point must be marked on each well via notching or indelible marker.
9. Wells should be developed to a turbid-free discharge.
10. Details for an Unconsolidated Aquifer Well are shown on Figure 3.

# MONITOR WELL SPECIFICATIONS FOR CONFINED UNCONSOLIDATED AQUIFERS

1. The construction of all monitoring wells shall be in accordance with the requirements of N.J.A.C.7:9D-2.2 et seq.
2. Minimum screen and riser pipe inner diameter is 2 inches.
3. The use of glue or solvents is prohibited in the installation of well screens, riser pipes and well casing.
4. In order to prevent any induced interconnection between the overburden/weathered bedrock and competent bedrock, the well screen shall not extend across the aforementioned interface.
5. Wells must have a filter pack installed.
6. When grouting the annular space directly above a filter pack, the grout should be discharged horizontally from the tremie pipe.
7. the locking cap must be made of steel.
8. A New Jersey licensed surveyor must survey top of the innermost casing (excluding cap) to the nearest 0.01 foot. The survey point shall be the highest point of the casing. If the casing is level, the survey point shall be established on the northern side of the casing. The survey point must be marked on each well via notching or indelible marker.
9. Wells should be developed to a turbid-free discharge.
10. Details for a Confined Unconsolidated Aquifer Well are shown on Figure 4.

From NJDEP "Field Sampling Procedures Manual" (August 2005)

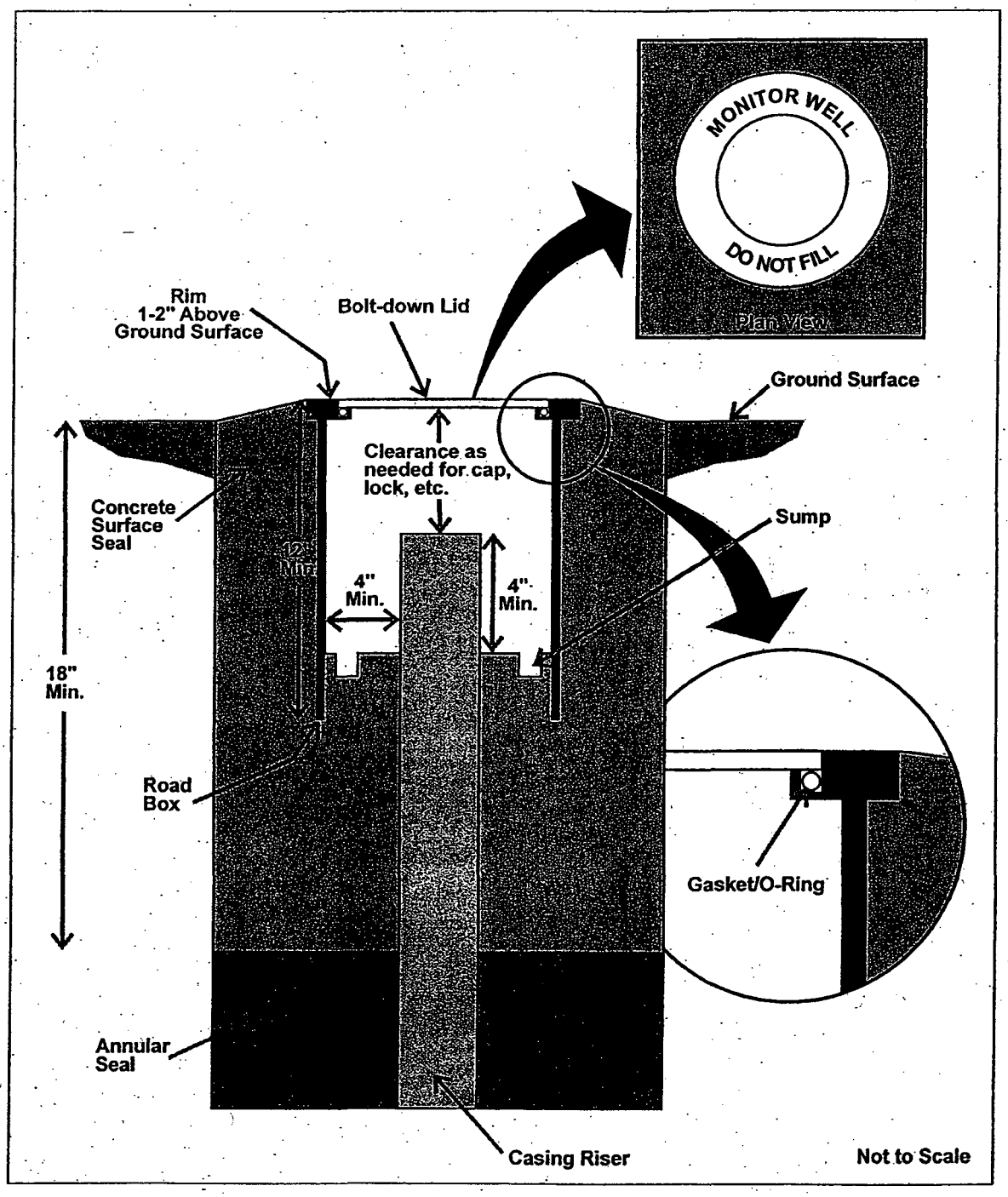



Figure 1. Typical Flush-Mount Completion

From NJDEP "Field Sampling Procedures Manual" (August 2005)

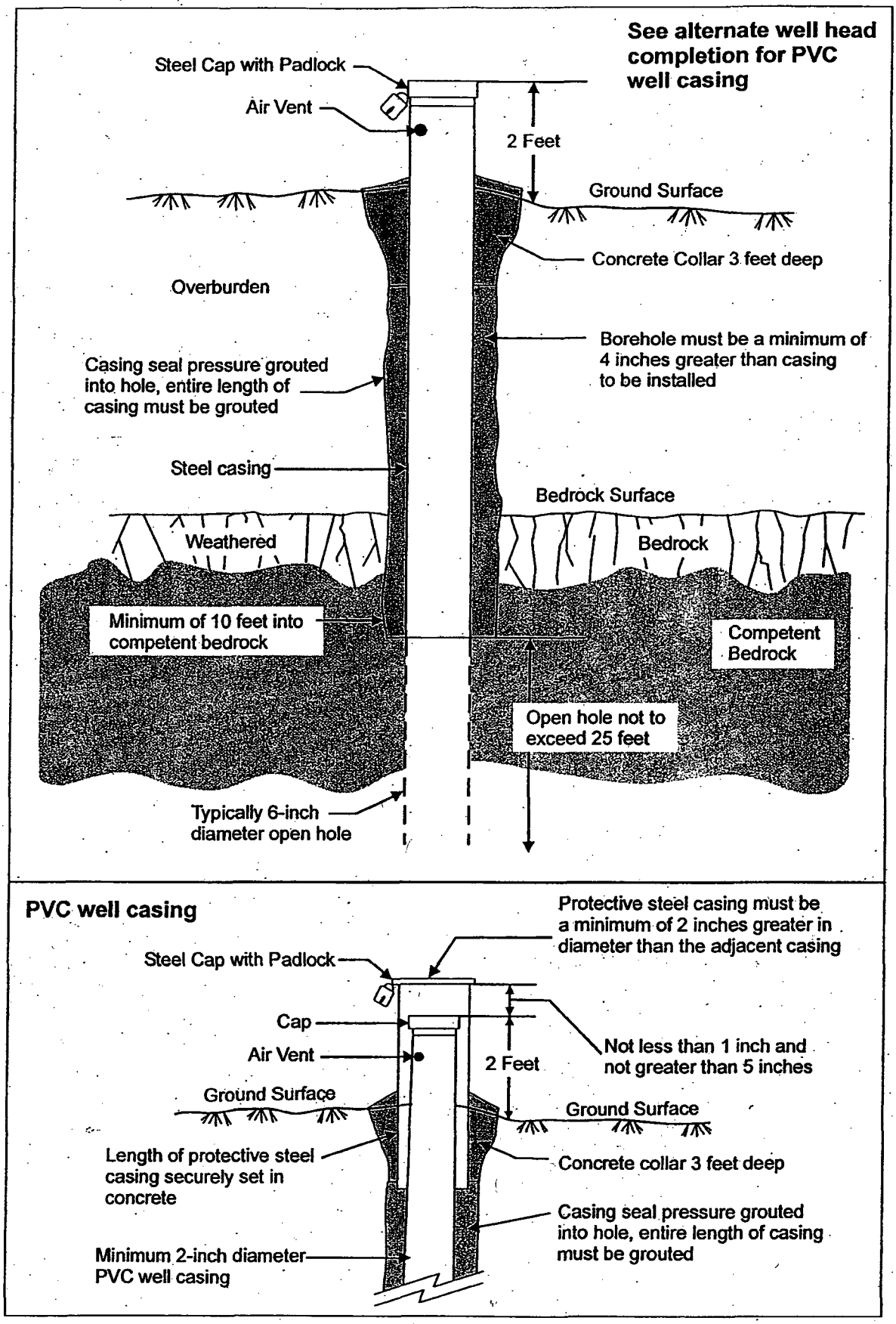



Figure 2. Bedrock Formation Well

From NJDEP "Field Sampling Procedures Manual" (August 2005)

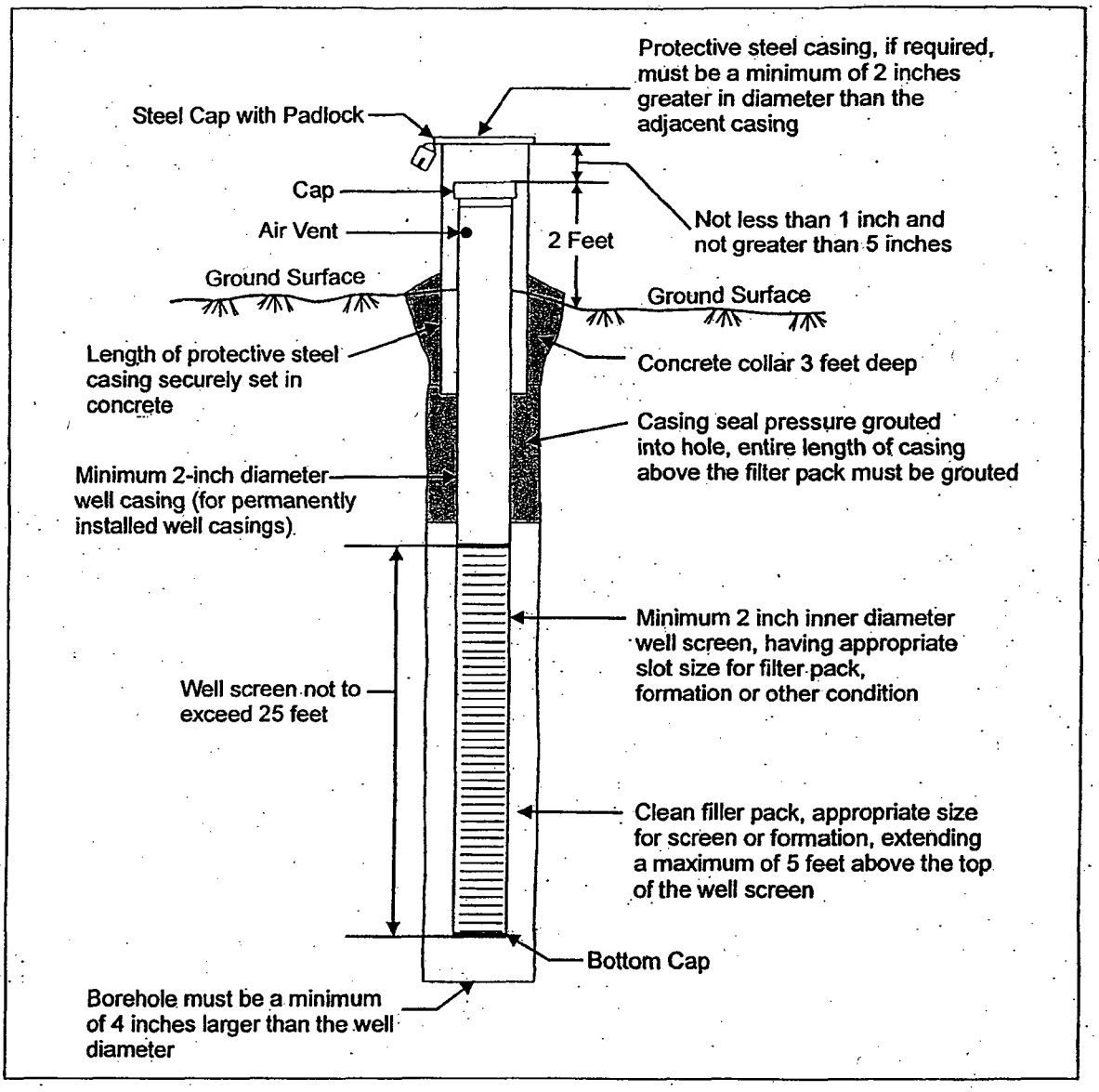



Figure 3. Unconsolidated Aquifer

From NJDEP "Field Sampling Procedures Manual" (August 2005)

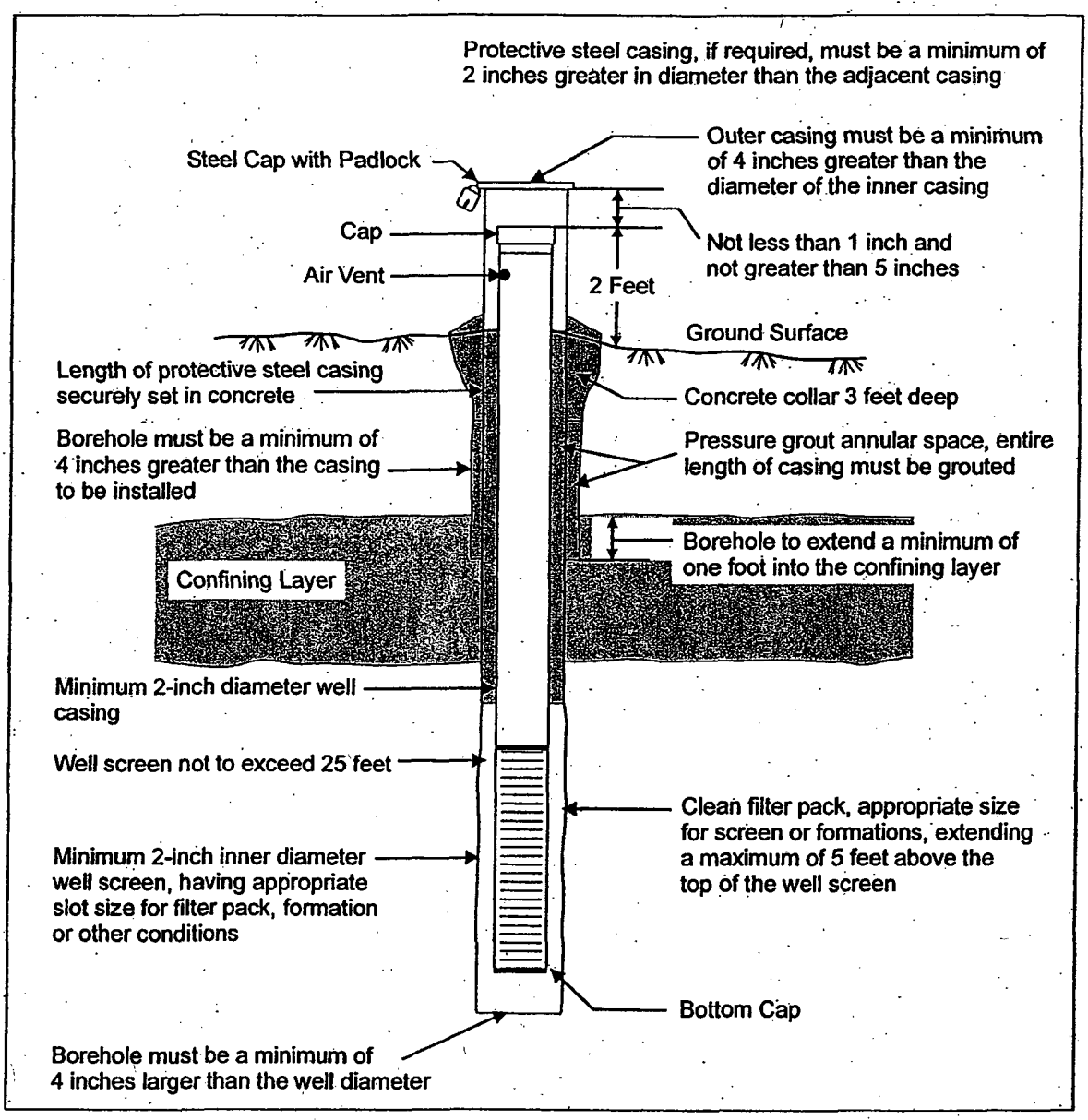



Figure 4. Confined Unconsolidated Aquifer Well

# LABORATORY SOPs

# LABORATORY
# STANDARD OPERATING PROCEDURES

HydroQual, Inc. will be utilizing the services of the following laboratories:

STL Edison, Inc. Edison, New Jersey (NJDEP LAB CERT # 12028)

Please find attached the laboratory Standard Operating Procedures for the analytical parameter methods that will be used to chemically evaluate various media as part of the OU-3 investigation.

## 1. SCOPE AND APPLICATION

1.1. Method 624 has been designed for the determination of volatile organic compounds in wastewater samples by purge and trap GC/MS techniques. The method is applicable to the compounds listed in Table 1. Actual target compound lists are determined through regulatory or project specifications. Method performance criteria for each target analyte will be determined prior to sample analysis.

**TABLE 1: METHOD ANALYTES**

| PARAMETER | CAS# |
|---|---|
| Benzene | 71-43-2 |
| Bromodichloromethane | 75-27-4 |
| Bromoform | 75-25-2 |
| Bromomethane | 74-83-9 |
| Carbon tetrachloride | 56-23-5 |
| Chlorobenzene | 108-90-7 |
| Chloroethane | 75-00-3 |
| 2-Chloroethylvinyl ether | 110-75-8 |
| Chloroform | 67-66-3 |
| Chloromethane | 74-87-3 |
| Dibromochloromethane | 124-48-1 |
| 1,2-Dichlorobenzene | 95-50-1 |
| 1,3-Dichlorobenzene | 541-73-1 |
| 1,4-Dichlorobenzene | 106-46-7 |
| 1,1-Dichloroethane | 75-34-3 |
| 1,2-Dichloroethane | 107-06-2 |
| 1,1-Dichloroethene | 75-35-4 |
| trans-1,2-Dichloroethene | 156-60-5 |
| 1,2-Dichloropropane | 78-87-5 |
| cis-1,3-Dichloropropene | 10061-01-5 |
| trans-1,3-Dichloropropene | 10061-02-6 |
| Ethylbenzene | 100-41-4 |

| PARAMETER | CAS# |
| --- | --- |
| Methylene chloride | 75-09-2 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 |
| Tetrachloroethene | 127-18-4 |
| Toluene | 108-88-3 |
| 1,1,1-Trichloroethane | 71-55-6 |
| 1,1,2-Trichloroethane | 79-00-5 |
| Trichloroethene | 79-01-6 |
| Trichlorofluoromethane | 75-69-4 |
| Vinyl chloride | 75-01-4 |

1.2. In addition to the analytes listed in Table 1, this method can be used for other volatile organic compounds, provided all preliminary performance data has been achieved. Water-soluble compounds can be included in this method, but detection limits will be higher due to poor purging efficiency.

1.3. Detection limits are derived annually as per Appendix B to Part 136 of EPA 40CFR. Non-routine compounds will be reported to the lowest calibration standard.

1.4. This method can be used as a screen for Acrolein and Acrylonitrile, however, the preferred analytical method for these compounds is Method 603.

## 2. METHOD SUMMARY

2.1. Method 624 is used to determine volatile organic compounds in wastewater samples. Purge and trap techniques are used to introduce the sample to the GC/MS system. An aliquot of sample containing internal standard and surrogate spiking solution is purged with helium in a closed sparging vessel. The volatile compounds are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatiles are trapped. After purging is complete, the sorbent column is heated and backflushed with helium to desorb the volatiles onto a gas chromatograph column. The gas chromatograph is temperature programmed to separate the

volatile organic compounds, which are then detected with a mass spectrometer.

## 3. INTERFERENCES

3.1 This method is susceptible to contamination from a number of sources, including organic solvents used in other laboratory procedures, impurities in the purge gas, improper cleaning of syringes or purge vessels, and carryover from high level samples. Samples can be contaminated by the diffusion of volatile organics through the septum during shipment or storage. Steps have been taken to ensure that these potential problems are eliminated from the laboratory.

3.2 The volatile laboratory has been moved to a separate building, away from the organic extraction area where large quantities of organic solvents are used. No organic solvents are used or stored in the volatile laboratory.

3.3 The helium used as purge gas passes through a solvent trap prior to its inlet into the purge and trap units.

3.4 A trip blank prepared from organic-free reagent water is carried through the sampling, storage and analysis of each group of samples to check for such contamination.

3.5 Individual samples are each handled with a unique syringe that has been baked in a drying oven at 105°C to ensure the absence of volatile compounds.

3.6 Purge vessels are removed from the autosampler unit after each use, rinsed, baked, returned to the unit and pre-purged before the next use.

3.7 Carryover can occur anytime a high level sample is analyzed. Screening procedures are employed to ensure that a sample is analyzed at an appropriate dilution to minimize potential carryover. When a high level sample is analyzed, it is followed by the analysis of a reagent water blank. If another sample was analyzed after the high level sample, this sample is inspected carefully for signs of carryover. If this sample does not contain any of the compounds found in the high level sample, the system can be considered contamination free.

3.8 The analytical system is checked daily with the analysis of a method blank. This blank must meet all quality control criteria for the method before sample analysis may take place.

4. APPARATUS AND MATERIALS

4.1 Microsyringes. 10 ul to 1000 ul.

4.2 Syringes. 5ml gas-tight.

4.3 Volumetric flasks. Class "A" glassware, 10 ml, 50 ml, and 100 ml.

4.4 VOA vials. 40-ml glass with PTFE –faced septum.

4.5 Vials. 2ml amber glass with screw cap with Teflon-faced septa.

4.6 Purge and trap unit. Consists of three parts: the sample purge unit, the trap, and the concentrator.

4.7 Purge and trap units from several different manufacturers are used. Purge and trap units used include the Tekmar 2016 automatic sampler/2000 concentrator, the OI Analytical 4551 automatic sampler/OI Analytical 4560 concentrator, and the Archon 5100A automatic sampler/ OI Analytical 4560 concentrator.

4.7.1 The purge chambers of each unit are designed to accept a 5 ml sample with a water column at least 3 cm deep. The headspace above the water has a volume less than 15 ml. The purge gas is introduced no more than 5 mm from the base of the water column. The purge gas passes through the water column as finely divided bubbles, each with a diameter of less than 3mm at the origin.

4.7.2 The VOCARB 3000 (Supelco) is used with the Tekmar concentrator. The trap is 25 cm long with an inside diameter of 0.105 inches. The trap is packed with 10.0 cm Carbopack B, 6.0 cm Carboxin 1000, and 1 cm Carboxin 1001.

4.7.3 The OI Analytical purge trap #10 is used with the OI 4560 concentrator. The trap is 25 cm long and has an inside diameter of 0.105 inches. The trap is packed to contain the following absorbents: Tenax/silica gel/ carbon molecular sieve.

4.7.4 Alternate traps may be used provided the adsorption and desorption characteristics are equivalent to those of the trap recommended by the method.

4.7.5 The concentrator of each unit is capable of rapidly heating the trap to 260°C and holding at that temperature for the duration of the desorb time.

4.8 Gas chromatograph. HP 5890 equipped with temperature programming capability.

4.9 GC column. 75 M long x 0.53 mm ID, J&W DB-624 capillary column with 3 um film thickness.

4.10 Injection port liners. HP 18740-80200 or equivalent.

4.11 Mass Spectrometer (HP5970B/5971/5972): scanning from 35-300 amu every 0.9 seconds, utilizing 70 volts (nominal) electron energy in the electron ionization mode and producing a mass spectrum which meets all EPA performance criteria (see sec.5.3) when 50 ng of 4-Bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

4.12 GC/MS Interface: glass jet separator with fused silica transfer lines heated to 180°C

4.13 Data system.

4.13.1 HP Chemstation II for data acquisition.

4.13.2 HP UNIX based TARGET software for data processing.

5. REAGENTS

5.1 Organic free reagent water. Distilled water purchased from Poland Spring.

5.2 Methanol. Ultra Resi-Analyzed, purge and trap grade, purchased from JT Baker. (Cat # 9077-02)

6. STANDARDS

6.1 Stock standards are purchased from Supelco Inc., Accustandard, or Protocol as certified mixes or prepared from neat.

6.2 Secondary dilution standards are prepared as follows:

**TABLE 2: STANDARD PREPARATION**

| Calibration Standard | Volume | Concentration | Concentration of Mix | Total Vol. in Methanol (TV/M) |
| --- | --- | --- | --- | --- |
| Gas Mix* | 500ul | 2000ppm | 50ppm | 20 ml TV/M<br>19.5 ml MeOH |
| 624 Mix 1* | 500ul | 2000ppm | 50ppm | 20 ml TV/M<br>19.5 ml MeOH |
| 8260 Mix 5*<br>Mix 6*<br>CEVE* | 500ul<br>500ul<br>500ul | 2000ppm/<br>varied | 50ppm/<br>varied | 20 ml TV/M<br>18.5 ml MeOH |
| 8260 Mix 7* | 2000ul | varied | varied | 20 ml TV/M<br>18 ml MeOH |
| Gas Mix BS<br>CEVE BS | 500ul<br>500ul | 2000ppm | 50ppm | 20 ml TV/M<br>19 ml MeOH |
| 624 Mix 1 BS | 500ul | 2000ppm | 50ppm | 20 ml TV/M<br>19.5 ml MeOH |
| SURR | 400ul | 2500ppm | 50ppm | 20 ml TV/M<br>19.6 ml MeOH |

| TABLE 2: STANDARD PREPARATION | | | | |
|---|---|---|---|---|
| **Calibration Standard** | **Volume** | **Concentration** | **Concentration of Mix** | **Total Vol. in Methanol (TV/M)** |
| CLP IS (Archon)<br>SURR | 750ul<br>300ul | 1000ppm<br>2500ppm | 150ppm | 5.0 ml TV/M<br>4.0 ml MeOH |
| | | | | |

6.3 All standards flagged with an * are also prepared from a second source of stock standards for use in spiking the QC check sample.

6.4 Pre-made 15ppm IS/SURR is purchased from Supelco.

6.5 Frequency of standard preparation

6.5.1 All standards are monitored frequently with the analysis of calibration verification standards. Any standard exhibiting more than a 20% drift from the initial calibration should be replaced. Gas standards are typically replaced weekly. Non-gas standards must be replaced monthly.

6.6 Stock standards and working solutions are stored in separate refrigerators, stock standards at 4°C and working standards at −10 to −20° C.

## 7. PRESERVATION AND HANDLING

7.1 All samples are collected in 40 ml VOA vials and preserved to a pH $<2$.

7.2 All samples must be analyzed within 14 days of sample collection.

7.3 If a sample is unpreserved, analysis must be completed within 7 days.

7.4 All samples are protected from light and stored at 4°C from time of receipt to analysis.

## 8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2 The analyst should wear the appropriate personal protective equipment including lab coat, safety eyewear, and gloves.

8.3 Any questions pertaining to safety issues or procedures should be brought to the department manager or Edison Safety Officer.

8.4 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

8.5 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
| --- | --- | --- | --- |
| Methanol | Flammable<br>Poison<br>Irritant | 200 ppm-TWA | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 9. PROCEDURE

9.1 Instrument operating parameters are established prior to calibration and will remain the same throughout the entire analytical procedure.

**INSTRUMENT OPERATING PARAMETERS**

| | |
| --- | --- |
| **Purge and trap unit** | |
| Purge Time | 11 minutes |
| Dry Purge | 1 Minutes |
| Purge Gas | Helium |
| Purge Flow | 40-45 ml/min |
| Purge Temp | Water - Ambient |
| Trapping Temp | Ambient, <30°C |
| Desorb Time | 1 Minute |
| Desorb Temp | VOCARB: 260°C, #10: 190°C |
| **Gas chromatograph** | |
| Injector | 180°C |
| Carrier Gas | Helium |
| Carrier Flow | 6 ml/min |
| Oven Program | 35 - 250°C with 2 ramps |
| Run Time | 22 Minutes |
| **Mass Spectrometer** | |
| Electron Energy | 70 volts (nominal) |
| Mass range | 35-260 AMU |
| Scan time | 0.9 sec./scan |
| Source Temp | 200°C |
| Separator Temp | 180°C |

9.2 Instrument tuning

9.2.1 The GC/MS tune is checked at the beginning of each 24 hour shift (prior to the injection of calibration standards or blanks) by injecting 50ng BFB (1ul of SURR solution) to meet the following criteria:

**TABLE 3: BFB Key Ions and Abundance Criteria**

| Mass | Ion Abundance Criteria |
| --- | --- |
| 50 | 15.0-40.0 percent of the base peak |
| 75 | 30.0-60.0 percent of the base peak |
| 95 | Base peak, 100% relative abundance |
| 96 | 5.0-9.0 percent of the base peak |
| 173 | Less than 2.0% of mass 174 |
| 174 | Greater than 50% of the base peak |
| 175 | 5.0-9.0 percent of mass 174 |
| 176 | Greater than 95.0% but less than 101% of mass174 |
| 177 | 5.0-9.0 percent of mass 176 |

9.2.2 Evaluate BFB by averaging the top three scans and subtracting a single scan prior to the elution of the BFB peak. The BFB may also be passed by using any of the top three single scans.

9.3 Initial calibration

9.3.1 Once the BFB has been injected and met the criteria in Section 9.2.1, calibrate the GC/MS system.

9.3.2 Prior to performing any purge and trap analysis, prepare each system in the following manner:

9.3.2.1 Equip the Tekmar 2000/2016 system with clean glassware that has been baked in a drying oven at 105°C overnight. Pre-purge each position for 6 minutes. Condition the trap at 260°C for 15 minutes while backflushing with helium. Also condition the GC column at 200°C for 15 minutes.

9.3.2.2 Condition the OI Analytical 4560 concentrator by baking the trap at 210°C for 12 minutes. Also condition the GC column by baking at 200°C.

9.3.2.3 Prepare the Archon by accessing the FLUSH menu on the Archon Autosampler. Rinse the syringe barrel with two heated 6mL portions of rinse

water. Turn off the helium switch, and fill the water reservoir with reagent water. Visually inspect the standard vial and fill with the appropriate internal standard/surrogate mix. Turn the helium switch back on. Prime the standard loop by accessing the SYSTEM/ MAINTENANCE/ STANDARD CONTROL menu. Empty the waste reservoir.

9.3.2.4 Prepare the OI 4551 by adding internal standard/surrogate solution to the SIM spiker, fill the water reservoir, and empty the waste.

9.3.3 Prepare aqueous calibration standards at five concentration levels for each parameter to be measured by adding the following amounts of each working standard to a 5mL syringe of reagent water:

**TABLE 4: INITIAL CALIBRATION PREP.**

| STANDARD | 5ug/L | 10ug/L | 20ug/L | 50ug/L | 200ug/L |
| --- | --- | --- | --- | --- | --- |
| IS/SURR(15ppm) | 10uL | 10uL | 10uL | 10uL | 10uL |
| 624 Mix 1 | 0.5uL | 1uL | 2uL | 5uL | 20uL |
| Gas Mix | 0.5uL | 1uL | 2uL | 5uL | 20uL |
| Mix 5/6/CEVE | 0.5uL | 1uL | 2uL | 5uL | 20uL |
| 8260 Mix 7 | 1uL | 2uL | 3uL | 4uL | 5uL |

9.3.4 Load the aqueous calibration standard into a purge vessel and begin purging. Analyze as in section 9.8.5.

9.3.5 If the calibration is to run on the OI 4551 or Archon autosampler, prepare the calibration standards in 50mL volumetric flasks. Multiply the amount of all standards in the calibration prep table by 10. Do not add internal standard/surrogate mix since it will be added by the autosampler. Pour the aqueous calibration standards into 40mL VOA vials and load on to the autosampler carrousel.

9.4 Evaluation of the initial calibration

9.4.1 Internal standard calibration will be used for this method.

9.4.2 Each target analyte, surrogate, and internal standard will be quantitated based on the integrated area of a characteristic ion or quant ion. See Table 5 for quant ions for target analytes.

**TABLE 5: Characteristic Ions of Volatile Organic Compounds**

| Parameter | Primary ion | Secondary ion |
| --- | --- | --- |
| Chloromethane | 50 | 52 |
| Bromomethane | 94 | 96 |
| Vinyl chloride | 62 | 64 |
| Chloroethane | 64 | 66 |
| Methylene chloride | 84 | 49,51,86 |
| Acetone | 43 | 58 |
| Carbon disulfide | 76 | 78 |
| 1,1-Dichloroethene | 96 | 61,98 |
| 1,1-Dichloroethane | 63 | 65,83,85,98,100 |
| 1,2-Dichloroethene | 96 | 61,98 |
| Chloroform | 83 | 85 |
| 1,2-Dichloroethane | 62 | 64,100,98 |
| 2-Butanone | 72 | 57 |
| 1,1,1-Trichloroethane | 97 | 99,117,119 |
| Carbon tetrachloride | 117 | 119,121 |
| Vinyl acetate | 43 | 86 |
| Bromodichloromethane | 83 | 85 |
| 1,1,2,2-Tetrachloroethane | 83 | 85,131,133,166 |
| 1,2-Dichloropropane | 63 | 65,114 |
| trans,-1,3-Dichloropropene | 75 | 77 |
| Trichloroethene | 130 | 95,97,132 |
| Dibromochloromethane | 129 | 208,206 |
| 1,1,2-Trichloroethane | 97 | 83,85,99,132,134 |
| Benzene | 78 | -- |
| cis-1,3-Dichloropropene | 75 | 77 |
| Bromoform | 173 | 171,175, |
| 2-Hexanone | 43 | 58,100 |
| 4-Methyl-2-Pentanone | 43 | 58,100 |
| Tetrachloroethene | 164 | 129,131,166 |

**TABLE 5: Characteristic Ions of Volatile Organic Compounds**

| Parameter | Primary ion | Secondary ion |
| --- | --- | --- |
| Toluene | 92 | 91 |
| Chlorobenzene | 112 | 114 |
| Ethylbenzene | 106 | 91, |
| Styrene | 104 | 78,103 |
| Total Xylenes | 106 | 91 |
| Surrogate Standards | | |
| 4-Bromofluorobenzene | 95 | 174,176 |
| 1,2-Dichloroethane-d4 | 65 | 102, 104 |
| Toluene-d8 | 98 | 70,100 |
| Internal Standards | | |
| Bromochloromethane | 128 | 49,130 |
| 1,4-Difluorobenzene | 114 | 88,63 |
| Chlorobenzene-d5 | 117 | 82,119 |

9.4.3 Calculate relative response factors (RRF) for each compound using the equation below. This calculation is performed automatically using the Target Software package.

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:
As = Peak area (or height) of the analyte or surrogate.
Ais = Peak area (or height) of the internal standard.
Cs = Concentration of the analyte or surrogate.
Cis = Concentration of the internal standard.

9.4.4 Calculate the relative standard deviation (RSD) of the five RRFs for each compound in the calibration curve.

9.4.5 If the RSD is <35% for the analytes listed in Table 1, the average RF will be used for all calculations.

9.4.6 Additional compounds included in the initial calibration will use 40% RSD as an advisory limit.

9.4.7 If the RSD for any compound listed in Table 1 is > 35%, an alternate mode of calibration can be used. Plot a calibration curve of response ratios, As/Ais vs RF.

9.5 Calibration verification

9.5.1 Calibration verification must be performed every 24 hours of instrument operation or at the beginning of an analytical sequence to verify the initial calibration. The calibration verification consists of a BFB instrument tune check, and the analysis of a QC check sample.

9.5.1.1 Tune Verification. Follow the procedure for the instrument tune described in section 9.2, using a 50 ng injection of BFB. If the tune cannot be verified analysis must be stopped, corrective action taken and a return to "control" demonstrated before continuing with the calibration verification process.

9.5.1.2 Calibration Verification. Analyze the QC check sample immediately after a BFB that meets criteria. The QC check sample must be prepared using stock standards other than those used for the initial calibration. Prepare the QC check sample in 5mL reagent water at a concentration of 20 ug/l as in Table 4.

9.5.1.2.1 If the QC check is to run on the OI or Archon autosamplers, prepare the standard in a 50 ml volumetric flask. Multiply all volumes in Table 4 by 10, and add to the flask containing reagent

water. Do not add internal standard/ surrogate solution as it will be added by the autosampler. Mix the contents of the flask by inverting three times. Pour into a 40-ml VOA vial.

9.5.2 Evaluation of QC check sample

9.5.2.1 For each parameter compare the response (Q) with the corresponding acceptance criteria in Table 6.

**TABLE 6: ACCEPTANCE CRITERIA FOR QC CHECK SAMPLE**

| Parameter | Range for Q (ug/l) |
| --- | --- |
| Benzene | 2.8 - 27.2 |
| Bromodichloromethane | 3.1 - 26.9 |
| Bromoform | 4.2 - 25.8 |
| Bromomethane | 2.8 - 37.2 |
| Carbon tetrachloride | 4.6 - 25.4 |
| Chlorobenzene | 3.2 - 26.8 |
| Chloroethane | 7.6 - 32.4 |
| 2-Chloroethylvinyl ether | D - 44.8 |
| Chloroform | 13.5 - 26.5 |
| Chloromethane | D - 40.8 |
| Dibromochloromethane | 13.5 - 26.5 |
| 1,2-Dichlorobenzene | 12.6 - 27.4 |
| 1,3-Dichlorobenzene | 14.6 - 25.4 |
| 1,4-Dichlorobenzene | 12.6 - 27.4 |
| 1,1-Dichloroethane | 14.5 - 25.5 |
| 1,2-Dichloroethane | 13.6 - 26.4 |
| 1,1-Dichloroethene | 10.1 - 29.9 |
| trans-1,2-Dichloroethene | 13.9 - 26.9 |
| 1,2-Dichloropropane | 6.8 - 33.2 |
| cis-1,3-Dichloropropene | 4.8 - 35.2 |
| trans-1,3-Dichloropropene | 10 - 30 |
| Ethylbenzene | 11.8 - 28.2 |
| Methylene chloride | 12.1 - 27.9 |

**TABLE 6: ACCEPTANCE CRITERIA FOR QC CHECK SAMPLE**

| Parameter | Range for Q (ug/l) |
| --- | --- |
| 1,1,2,2-Tetrachloroethane | 12.1 - 27.9 |
| Tetrachloroethene | 14.7 - 25.3 |
| Toluene | 14.9 - 25.1 |
| 1,1,1-Trichloroethane | 15 - 25 |
| 1,1,2-Trichloroethane | 14.2 - 25.8 |
| Trichloroethene | 13.3 - 26.7 |
| Trichlorofluoromethane | 9.5 - 30.4 |
| Vinyl chloride | 0.8 - 39.2 |

9.5.2.2 Any additional compounds not listed in Table 6 will use 40% D as an advisory limit.

9.5.2.3 Repeat the QC check for any parameters that fail. If the second check fails, a new initial calibration must be performed.

9.5.2.4 Internal standard retention time is evaluated immediately after acquisition. The retention times of the internal standards from the calibration check must be within ± 30 seconds of the internal standards from the mid-point standard of the initial calibration, or from the most recent calibration verification standard.

9.5.2.5 Internal standard area response is also evaluated immediately after acquisition. The response (area count) of each internal standard in the calibration verification standard must be within 50 - 100% of its corresponding internal standard in the mid-level calibration standard of the initial calibration curve. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometer system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-

analysis of samples analyzed while the system was malfunctioning is required.

9.6 Blank spike analysis

9.6.1 After a successful calibration, analyze a blank spike.

9.6.2 The blank spike is also prepared from stock standards other than those used for the initial calibration.

9.6.3 Prepare a blank spike at a concentration of 20 ug/l as follows: to a 5 ml syringe containing reagent water, add 2 ul of 50 ppm 624 Mix 1 BS, 2 ul of 50 ppm Gas Mix BS, and 10 ul of 15 ppm IS/SURR solution.

9.6.4 If the blank spike is to run on the OI or Archon autosampler, add 20 ul of 50 ppm 624 Mix 1 BS and 20 ul of 50 ppm Gas Mix BS to a 50 ml flask containing reagent water. Do not add surrogate as it will be added by the autosampler prior to purging. Mix the contents of the flask by inverting three times. Pour into a 40-ml VOA vial.

9.6.5 Evaluation of the blank spike

9.6.5.1 For each parameter, compare the recovery (P) with the corresponding acceptance criteria in Table 7.

**TABLE 7: ACCEPTANCE CRITERIA FOR BLANK SPIKE**

| Parameter | Range for P (%) |
| --- | --- |
| Benzene | 37 - 151 |
| Bromodichloromethane | 35 - 155 |
| Bromoform | 45 - 169 |
| Bromomethane | D - 242 |
| Carbon tetrachloride | 70 - 140 |
| Chlorobenzene | 37 - 160 |
| Chloroethane | 14 - 230 |
| 2-Chloroethylvinyl ether | D - 305 |

**TABLE 7: ACCEPTANCE CRITERIA FOR BLANK SPIKE**

| Parameter | Range for P (%) |
| --- | --- |
| Chloroform | 51 - 138 |
| Chloromethane | D - 273 |
| Dibromochloromethane | 53 - 149 |
| 1,2-Dichlorobenzene | 18 - 190 |
| 1,3-Dichlorobenzene | 59 - 156 |
| 1,4-Dichlorobenzene | 18 - 190 |
| 1,1-Dichloroethane | 59 - 155 |
| 1,2-Dichloroethane | 49 - 155 |
| 1,1-Dichloroethene | D - 234 |
| trans-1,2-Dichloroethene | 54 - 156 |
| 1,2-Dichloropropane | D - 210 |
| cis-1,3-Dichloropropene | D - 227 |
| trans-1,3-Dichloropropene | 17 - 183 |
| Ethylbenzene | 37 - 162 |
| Methylene chloride | D - 221 |
| 1,1,2,2-Tetrachloroethane | 46 - 157 |
| Tetrachloroethene | 64 - 148 |
| Toluene | 47 - 150 |
| 1,1,1-Trichloroethane | 52 - 162 |
| 1,1,2-Trichloroethane | 52 - 150 |
| Trichloroethene | 71 - 157 |
| Trichlorofluoromethane | 17 - 181 |
| Vinyl chloride | D - 251 |

9.6.5.2 If any compounds fail, repeat the blank spike. Do not proceed to the blank and sample analysis steps until a successful blank spike has been acquired.

9.7 Blank analysis

9.7.1 Analyze a system reagent blank every 24 hours of sample analysis or one per 20 field samples, whichever comes first, immediately after successful calibration and blank spike analysis.

9.7.2 Add 10 ul of 15ppm ISTD/SURR solution to a syringe containing 5 ml of reagent water, or fill a 40-ml VOA vial with reagent water for analysis using the OI or Archon autosampler. The autosamplers will add the internal standard/surrogate solution prior to purging.

9.7.3 Analyze the blank in the sample manner as the associated samples will be analyzed (section 9.8.5).

9.7.4 Evaluate the blank for QC acceptance criteria in section 10.6.

9.8 Sample analysis

9.8.1 Allow all samples to come to room temperature before analysis. Only after a successful tune, calibration, blank spike and blank can samples be run.

9.8.2 Screen all samples prior to analysis by GC/FID static headspace analysis using Method 5021 to determine appropriate dilution factors.

9.8.3 Prepare samples for analysis on the Tekmar 2016/2000 as follows:

9.8.3.1 Carefully pour the sample or standard into the barrel of a syringe, just short of overflowing. Replace the plunger, and compress the sample. Vent any air trapped in the syringe, and adjust the sample to volume.

9.8.3.2 Add 10 ul of 15 ppm IS/SURR spiking solution to the syringe.

9.8.3.3 Inject the aqueous sample into the purge vessel.

9.8.3.4 The process of taking an aliquot of sample destroys the validity of that sample for future volatile analysis. If there is only one vial of sample, immediately fill a second syringe and hold

it until it can be determined that the first analysis has been successful.

9.8.4 Prepare samples for analysis on the OI 4551/4560 or Archon autosamplers as follows:

9.8.4.1 Place the sample vials in the autosampler tray for automated purge and trap analysis. Edit the autosampler schedule to specify the appropriate start and stop locations. The sample vial is selected and a sampling needle is inserted through the septum. 5mL of sample is removed from the sample vial and transferred to the purge vessel. The Archon autosampler will add 1 ul of 150 ppm IS/SURR solution as the 5mL passes through the sample loop. The OI 4551 autosampler will add 10 ul of 15 ppm IS/SURR solution.

9.8.4.2 The process of using the OI 4551/4560 or Archon autosampler also destroys the validity of the sample by puncturing the septum. Any re-analysis should be done using second vial of sample. If only one vial exists, do not use this autosampler.

9.8.5 Purge the sample for 11 minutes.

9.8.6 After purging is complete, desorb the sample onto the GC column by rapidly heating the trap to 260°C for VOCARB, 190°C for #10 and backflushing it with helium.

9.8.7 Begin the GC temperature program and data acquisition.

9.8.8 Recondition the trap by baking for 12 minutes at 260°C for VOCARB, 210°C for #10.

9.8.9 Cool the trap to (<31°C). The trap is now ready for the next sample.

9.8.10 Transfer data to network, and process using TARGET software.

9.8.11 Any sample exhibiting target analytes with concentrations greater than the highest calibration standard must be diluted. All dilutions are made either in a volumetric flask or directly in the 5mL syringe.

9.8.11.1 Aliquots of less than 1 ul are not permitted. For dilutions requiring less than 1 ul of sample, an intermediate dilution must be made.

9.8.11.2 All sample dilutions should keep the concentrations of target analytes in the upper half of the calibration range.

9.8.11.3 All steps must be performed quickly to minimize the loss of volaltiles due to handling.

9.8.11.4 Calculate the approximate volume of organic-free reagent water to be added to the syringe or volumetric flask, and add slightly less than this quantity of organic-free reagent water.

9.8.11.5 Inject the appropriate volume of the original sample into the syringe or flask. If in a flask, dilute the sample to volume with organic-free reagent water. Cap the flask, invert three times. Pour into a 40mL VOA vial.

9.8.11.6 Load the samples into purge chambers, or place VOA vials in autosampler tray.

9.9 Data processing

9.9.1 Prior to processing any standards or samples, target compound methods and sublists must be assembled in the Target system. These methods are required for data processing. They include compound names, retention time data, quantitation ions, qualitative identification ions, and the assigned internal standard for qualitative and quantitative identification.

9.9.2 Key data is manually entered the first time a method is used for data processing. Processing data using a method automatically generates response factor data and updates retention information.

9.9.3 Data is transferred from the acquisition PC to the network for processing with TARGET software.

9.9.4 Each data file is checked for correct information including sample number, job number, QA batch, dilution factor, initial volume, and final volume.

9.9.5 Each sample is checked against a department work list for the correct sublist of target analytes.

9.9.6 Each data file is processed using response factors from the most recent initial calibration.

9.10 Qualitative identification of target compounds is based on retention time, and mass spectral comparison with characteristic ions in the target compound list. The reference mass spectrum is taken from a standard of the target compound analyzed by the same method. The characteristic ions are the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

9.10.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.

9.10.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

9.10.3 The relative intensities of the characteristic ions agree within 20% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 30% and 70%.)

9.10.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are identified as isomeric pairs.

9.10.5 All target compounds are reported down to their calculated MDL.

9.11 Qualitative identification of non-target compounds is done using the most recent version of the Wiley library. The following guidelines are used for identifying non-target compounds:

9.11.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

9.11.2 The relative intensities of the major ions should agree within 20% of those found in the reference spectrum. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

9.11.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

9.11.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

9.11.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

9.12 Quantitative analysis for target compounds is performed by quantitation using the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of the analyte.

9.13 Determine the concentration using the response factor from the calibration technique employed in section 9.0.

9.14 Quantitative analysis for non-target compounds will be performed using a modified version of the calculation used for target analytes. Non-Target concentrations are calculated using total ion areas for the analyte and the internal standard, and the response factor for the analyte is assumed to be 1.0.

9.15 The resulting concentration is flagged indicating: (a) that the value is an estimate, and (b) which internal standard was used to determine the concentration. Use the nearest internal standard free of interferences.

## 10. QUALITY CONTROL

10.1 Initial demonstration of accuracy and precision

10.1.1 An initial demonstration of proficiency must be completed before sample analysis may begin.

10.1.2 Prepare a reference sample at a concentration of 20 ug/l from standard materials other than those used for calibration.

10.1.3 Analyze four replicates of the reference sample using the appropriate sample introduction technique combined with the determinative method.

10.1.4 Calculate the average recovery (x) in ug/l and the standard deviation (s) of the recoveries for each analyte.

10.1.5 Compare (x) and (s) for each analyte to the performance data found in Table 8.

**Table 8: Initial Demonstration of Accuracy and Precision**

| PARAMETER | Limit for (s) ug/L | Range for (x) ug/L |
| --- | --- | --- |
| Benzene | 6.9 | 15.2-26.0 |
| Bromodichloromethane | 6.4 | 10.1-28.0 |
| Bromoform | 5.4 | 11.4-31.1 |
| Bromomethane | 17.9 | D -41.2 |
| Carbon tetrachloride | 5.2 | 17.2-23.5 |
| Chlorobenzene | 6.3 | 16.4-27.4 |
| Chloroethane | 11.4 | 8.4-40.4 |
| 2-Chloroethylvinyl ether | 25.9 | D -50.4 |
| Chloroform | 6.1 | 13.7-24.2 |
| Chloromethane | 19.8 | D -45.9 |
| Dibromochloromethane | 6.1 | 13.8-26.6 |
| 1,2-Dichlorobenzene | 7.1 | 11.8-34.7 |
| 1,3-Dichlorobenzene | 5.5 | 17.0-28.8 |
| 1,4-Dichlorobenzene | 7.1 | 11.8-34.7 |
| 1,1-Dichloroethane | 5.1 | 14.2-28.5 |
| 1,2-Dichloroethane | 6.0 | 14.3-27.4 |
| 1,1-Dichloroethene | 9.1 | 3.7-42.3 |
| trans-1,2-Dichloroethene | 5.7 | 13.6-28.5 |
| 1,2-Dichloropropane | 13.8 | 3.8-36.2 |
| cis-1,3-Dichloropropene | 15.8 | 1.0-39.0 |
| trans-1,3-Dichloropropene | 10.4 | 7.6-32.4 |
| Ethylbenzene | 7.5 | 17.4-26.7 |
| Methylene chloride | 7.4 | D -41.0 |
| 1,1,2,2-Tetrachloroethane | 7.4 | 13.5-27.2 |
| Tetrachloroethene | 5.0 | 17.0-26.6 |
| Toluene | 4.8 | 16.6-26.7 |
| 1,1,1-Trichloroethane | 4.6 | 13.7-30.1 |
| 1,1,2-Trichloroethane | 5.5 | 14.3-27.1 |
| Trichloroethene | 6.6 | 18.6-27.6 |
| Trichlorofluoromethane | 10.0 | 8.9-31.5 |
| Vinyl chloride | 20.0 | D -43.5 |

10.2 Instrument tuning

10.2.1 Instrument tuning must be evaluated at the beginning of each 24 hour period with the analysis of 50ng of BFB. Ion abundance criteria in Table 3 must be achieved before proceeding to the calibration steps.

10.3 Initial calibration

10.3.1 All target analytes and surrogates for a particular analysis must be included in the initial calibration standards and calibration verification standards.

10.3.2 The lowest concentration calibration standard must be at a concentration level near but above the MDL. The other calibration standards define the working range of this method.

10.3.3 Calculate a response factor (RF) for each analyte at each concentration level by tabulating peak area response relative to the internal standard against concentration.

10.3.4 Calculate the relative standard deviation (RSD) of the RFs for each analyte.

10.3.5 If the RSD is less than 35%, the calibration is considered linear and the average RF can be used for quantitation.

10.3.6 For additional compounds analyzed by Method 624, a 40% RSD criteria is used.

10.3.7 If the RSD is greater than 35%, an alternate model of calibration must be used.

10.4 Calibration verification

10.4.1 The initial calibration must be verified every 24 hours with the analysis of a QC check sample.

10.4.2 The QC check sample is prepared at a concentration of 20 ug/l, and must be prepared from stock standards other than those used for the initial calibration.

10.4.3 Evaluate the QC check sample by comparing the response (Q) with the acceptance criteria in Table 6.

10.4.4 If any compound fails this criteria, analyze a second QC check sample.

10.4.5 If the second QC check fails, a new initial calibration must be performed.

10.5 Blank spike analysis

10.5.1 A blank spike is analyzed at a frequency of 1 per 20 samples (one per QA batch) or at least one per 20 field samples within an analytical sequence, immediately after calibration and before blank analysis.

10.5.2 The blank spike must be prepared from standard materials other than those used for the initial calibration.

10.5.3 The blank spike recoveries must fall in the acceptance ranges listed in Table 7.

10.5.4 If any compound fails these criteria, the blank spike must be re-analyzed.

10.6 Blank analysis

10.6.1 A method blank is analyzed once every 24 hours or one per 20 field samples, whichever comes first. The method blank is analyzed immediately after successful calibration and blank spike analysis and before any samples are analyzed.

10.6.2 The method blank must not have any target analytes above the MDL.

10.6.3 The method blank must not have any non-target compounds greater than 10% of the nearest internal standard.

10.6.4 The method blank must meet QC limits for acceptable surrogate recoveries.

10.6.5 The method blank must meet QC criteria for internal standard response and retention time.

10.7 Surrogate recoveries

10.7.1 Surrogate solution containing 1,2-Dichloroethane-d4, Toluene-d8, and Bromofluorobenzene is spiked into every blank, sample and QC sample at a concentration of 30 ug/l.

10.7.2 Surrogate recoveries are calculated for the blank, samples, and QC samples. Surrogate recovery is calculated as :

$$\frac{\text{Concentration found}}{\text{Concentration added}} \times 100 = \%\ \text{RECOVERY}$$

10.7.3 In house surrogate limits have been established by calculating the percent recovery (p) and the standard deviation(s) for each surrogate using 20 representative data points.

10.7.4 Recovery limits are generated by using (p) = ± 3(s).

10.7.5 New limits are generated annually.

10.7.6 Any blank, sample, or QC sample that fails to meet the criteria must be re-analyzed.

10.8 Internal standard monitoring

10.8.1 All standards, blanks, samples, and QC samples are monitored for internal standard area response and retention time.

10.8.2 Internal standard area response is evaluated immediately after acquisition. The response (area count) of each internal standard in the calibration verification standard must be within 50 - 100% of its corresponding internal standard in the mid-level calibration standard of the initial calibration curve, or the most recent calibration check standard. If the EICP area for

any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometer system must be inspected for malfunction and corrections made as appropriate.

10.8.3 Internal standard retention time is evaluated immediately after acquisition. The retention times of the internal standards must be within ±30seconds of the internal standards from the mid point standard of the initial calibration.

10.8.4 Any blank, sample, or QC sample that fails to meet these criteria must be re-analyzed.

10.9 Matrix spike/matrix spike duplicate

10.9.1 Matrix spike/matrix spike duplicate pairs are analyzed at a frequency of one set per 20 samples.

10.9.2 Prepare a matrix spike by adding 2 ul of 50 ppm 624 Mix 1 BS, 2 ul of 50 ppm Gas Mix BS, and 10 ul of 15 ppm IS/SURR Mix to a 5 ml sample.

10.9.3 The OI 4551 or Archon autosamplers can only be used for MS/MSD on samples requiring a dilution due to limited sample volume. Prepare these spikes in 50 ml volumetric flasks by adding 20 ul of 50 ppm 624 Mix 1 BS, and 20 ul of 50 ppm Gas Mix BS to the diluted sample.

10.9.4 Percent recovery (P) ranges for each analyte are listed in table 7.

10.9.5 If any method analyte falls outside the acceptable range, it may be attributed to matrix effects if the blank spike shows acceptable recovery for this analyte.

## 11. WASTE MANAGEMENT AND POLLUTION PREVENTION

### 11.1. WASTE MANAGEMENT:

11.1.1 The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

11.2. POLLUTION PREVENTION:

11.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

11.2.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

12. CALCULATIONS

12.1 Refer to the SOP for Organic Calculations, SOP Number OC03.

13. DEFINITIONS

13.1 Refer to document DEFDOC-04 for definitions.

14. METHOD PERFORMANCE

14.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

14.2 All MDL results are available on file.

## 15 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Technical acceptance criteria for sample analysis.

15.1.1 The samples must be analyzed on a GC/MS system meeting the initial calibration, continuing calibration and blank technical acceptance criteria.

15.1.2 The sample must be analyzed within the required holding time.

15.1.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

15.1.4 The percent recovery of each of the system monitoring compounds in the sample must be within the acceptance windows.

15.1.5 The retention time shift for each of the internal standards must be within +/- 0.50 minutes (30 seconds) between the sample and the most recent continuing calibration standard analysis.

15.1.6 After analyzing a sample that exceeds the initial calibration range the analyst must either analyze an instrument

blank (using the same purge inlet if using an auto sampler) which must meet technical acceptance criteria for blank analysis or monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the calibration range.

15.2 Corrective Action for Sample Analysis

15.2.1 *Samples must meet technical acceptance criteria before* reporting data.

15.2.2 Corrective action for failure to meet instrument performance checks, initial, continuing calibration and method blanks must be completed prior to sample analysis.

15.2.3 Corrective action for system monitoring compounds and internal standard compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

15.3 If any of the system monitoring compounds and internal standard compounds fail to meet acceptance criteria:

15.3.1 Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet acceptance criteria

15.3.2 Check the preparation of the internal standards and system monitoring compounds for concentration and expiration.

15.3.3 Verify that the instrument is operation correctly.

16 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments

defining the nature of the outage. If applicable, a Corrective Action Reports will be initiated in order to provide for investigation and follow-up.

## 17 REFERENCES

17.1 EPA 40 CFR, (7-1-94 edition), Part 136, Appendix A, Method 624.

| STL Edison Standard Operating Procedure<br>Title: EPA625, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)<br>Laboratory Director:<br>Technical Director:<br>QA Manager:<br>Department Manager:<br>File Location: F:\QAQC\SOPs\NELAC\NELAC SOPs 2004\110bnams\600\EPA62504.DOC | Revision Date:<br>06/24/04<br><br>SOP Number:<br>EPA62504<br>Revision 6<br><br>Page 1 of 25 |
|---|---|

## 1. SCOPE AND APPLICATION

1.1. The procedure that follows covers the GC/MS analysis of semi-volatile organic compounds found in municipal and industrial discharges. The compounds of interest are listed below:

| | | | |
|---|---|---|---|
| Acenaphthene | 83-32-9 | 4-Chloroaniline | 106-47-8 |
| Acenaphthene-$d_{10}$ (IS) | | 2-Chloronaphthalene | 91-58-7 |
| Acenaphthylene | 208-96-8 | 2-Chlorophenol | 95-57-8 |
| Acetophenone | 98-86-2 | 4-Chlorophenyl phenyl ether | 7005-72-3 |
| Aniline | 62-53-3 | Chrysene | 218-01-9 |
| Anthracene | 120-12-7 | Chrysene-$d_{12}$ (IS) | |
| Benzidine | 92-87-5 | Dibenz(a,h)anthracene | 53-70-3 |
| Benzoic acid | 65-85-0 | Dibenzofuran | 132-64-9 |
| Benz(a)anthracene | 56-55-3 | Benzo(g,h,I)perylene | 191-24-+2 |
| Benzo(b)fluoranthene | 205-99-2 | Benzo(a)pyrene | 50-32-8 |
| Benzo(k)fluoranthene | 207-08-9 | Phenol d6 (surr) | |
| Benzyl alcohol | 100-51-6 | Di-n-butyl phthalate | 84-74-2 |
| Bis(2-chloroethoxy)methane | 111-91-1 | 1,2-Dichlorobenzene | 95-50-1 |
| Bis(2-chloroethyl) ether | 111-44-4 | 1,3-Dichlorobenzene | 541-73-1 |
| Bis(2-chloroisopropyl) ether | 108-60-1 | 1,4-Dichlorobenzene | 106-46-7 |
| Bis(2-ethylhexyl) phthalate | 117-81-7 | 1,4-Dichlorobenzene-$d_4$ (IS) | |
| 4-Bromophenyl phenyl ether | 101-55-3 | 3,3'-Dichlorobenzidine | 91-94-1 |
| Butyl benzyl phthalate | 85-68-7 | 2,4-Dichlorophenol | 120-83-2 |
| 2,4-Dimethylphenol | 105-67-9 | Diethyl phthalate | 84-66-2 |
| Dimethyl phthalate | 131-11-3 | Hydroquinone | 123-31-9 |
| 4,6-Dinitro-2-methylphenol | 534-52-1 | Indeno(1,2,3-cd)pyrene | 193-39-5 |
| 2,4-Dinitrophenol | 51-28-5 | Isophorone | 78-59-1 |
| 2,4-Dinitrotoluene | 121-14-2 | 2-Methylnaphthalene | 91-57-6 |
| 2,6-Dinitrotoluene | 606-20-2 | 2-Methylphenol | 95-48-7 |
| 1,2-Diphenylhydrazine | 122-66-7 | 3-Methylphenol | 108-39-4 |
| Di-n-octyl phthalate | 117-84-0 | 4-Methylphenol | 106-44-5 |
| Fluoranthene | 206-44-0 | Naphthalene | 91-20-3 |
| Fluorene | 86-73-7 | Naphthalene-$d_8$ (IS) | |

| | | | |
|---|---|---|---|
| 2-Fluorobiphenyl (surr) | 321-60-8 | 2-Nitroaniline | 88-74-4 |
| 2-Fluorophenol (surr) | 367-12-4 | 3-Nitroaniline | 99-09-2 |
| Hexachlorobenzene | 118-74-1 | 4-Nitroaniline | 100-01-6 |
| Hexachlorobutadiene | 87-68-3 | Nitrobenzene | 98-95-3 |
| Hexachlorocyclopentadiene | 77-47-4 | Nitrobenzene-d5 (surr) | |
| Hexachloroethane | 67-72-1 | 2-Nitrophenol | 88-75-5 |
| N-Nitrosomethylethylamine | 10595-95-6 | 4-Nitrophenol | 100-02-7 |
| N-Nitrosodiphenylamine | 86-30-6 | Pyrene | 129-00-0 |
| N-Nitrosodi-n-propylamine | 621-64-7 | Pyridine | 110-86-1 |
| Pentachlorophenol | 87-86-5 | Terphenyl-$d_{14}$ (Surr) | 1718-51-0 |
| Perylene-$d_{12}$ (IS) | | 2,4,6-Tdbromophenol (surr) | 118-79-6 |
| Phenanthrene | 85-01-8 | 1,2,4-Trichlorobenzene | 120-82-1 |
| Phenanthrene-$d_{10}$ (IS) | | 2,4,5-Trichlorophenol | 95-95-4 |
| | | 2,4,6-Trichlorophenol | 88-06-2 |
| | | Phenol | 108-95-2 |

## 2. METHOD SUMMARY

This method is used for the analysis of semi-volatile base, neutral and acid organic compounds for wastewater, which are extracted from the sample matrix with an organic solvent. Sample extraction techniques are specified for each matrix in separate SOPs. An aliquot of sample containing surrogate spiking compounds is extracted with an organic solvent. The extract is concentrated on a steam bath to a suitable volume. Internal standards are added to the extract. A small aliquot of the extract is injected into a gas chromatograph (GC) equipped with a capillary column. The GC is temperature programmed to separate the compounds by boiling point, which were recovered during the extraction step. The effluent of the gas chromatograph is interfaced to a mass spectrometer (MS), which is used to detect the compounds eluting from the GC. The detected compounds are fragmented with an electron beam to produce a mass spectra which is characteristic of the compound introduced into the MS. Identification of target analytes is accomplished by comparing their mass spectra with the electron ionization spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion (quantitation ion) relative to an internal standard established through a five-point calibration. Specific calibration and quality control steps are included in the method that must be performed and must meet the specifications of Method 625.

## 3 DEFINITIONS

3.1 Refer to document DEFDOC-04 for definitions.

## 4 INTERFERENCES

4.1 Some compounds analyzed using this method are unstable or sensitive. Benzidine, for example, is easily oxidized during extraction. Hexachlorocyclopentadiene breaks down photochemically and can decompose from high temperatures, particularly in the injection port of the GC. Phenols are sensitive to active sites and can give a low response or exhibit poor chromatography by tailing. Therefore, it is important the GC is maintained in the best possible condition. See Section 10.2 for proper daily maintenance.

## 5 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 The analyst must wear a protective lab coat, safety glasses, and gloves when handling all samples, extracts, standards and solvents.

5.3 All questions pertaining to any safety procedure should be brought to the department manager or STL Edison Safety Officer.

5.4 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Methanol | Flammable Poison Irritant | 200 ppm-TWA | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| Methylene Chloride | Carcinogen Irritant | 25 ppm-TWA 125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

# 6 APPARATUS AND MATERIALS

## 6.1 GC/MS System

6.1.1 Gas Chromatograph: HP 5890 houses the capillary column. The GC provides a splitless injection port and allows the column to be directly coupled to the mass spectrometer. The oven is temperature programmable to meet the requirements of the method. An HP 7673 autosampler with a 10 ul syringe provides automatic injection of sample extracts while the instrument is unattended.

6.1.2 Column: 30 meter x 0.25 mm ID capillary column, Restek RTX-5MS, 0.25mm id, 0.5u film thickness. Catalog # 12638.

6.1.3 Mass Spectrometer: HP 5972 Mass Selective Detector (MSD), scanning from 35 to 450amu, every 1 second or less, utilizing 70 (nominal) electron volts in the electron impact (EI) ionization mode. The MS must be capable of producing a mass spectrum that meets all EPA criteria when 50ng of DFTPP (Decafluorotriphenylphosphine) is injected into the capillary column.

6.1.4 GC/MS Interface: Heated at 300°C, the capillary column is directly coupled to the mass spectrometer. The interface is capable of providing acceptable tuning criteria and allows for good compound response.

6.1.5 Data System: The data system consists of Mustang software for acquisition and Target for data processing. The computer is capable of handling many different tasks simultaneously. Sample extracts can be analyzed and manipulated in real-time, while sample data reports and library searches can be performed on previously run samples. Library searches utilize a NBS/Wiley Mass Spectral Library.

6.2 GC/MS Supplies

6.2.1 Injection port liners, splitless

6.2.2 Injection port septa

6.2.3 Injection port graphite seals

6.2.4 Pre-silanized glass wool (Supelco 2-0411 or equivalent)

6.2.5 Syringes, Assorted sizes 10ul - 1000ul; gas-tight

6.2.6 Bottles, 10 and 5ml amber screw cap with Teflon liner

6.2.7 Vials, 2ml amber screw cap with Teflon liner

6.2.8 Wheaton microvials 100ul or equivalent

6.2.9 Volumetric Flasks, Class A with ground glass stoppers (2ml - 50ml)

6.2.10 Balance, Analytical balance (ASP Model SP-180 or equivalent) capable of accurately weighing to 0.0001 gm.

## 7 REAGENTS

7.1 Methylene Chloride: Baker Resi-Analyzed, used for Organic Residue Analysis (P/N 9264-03 or equivalent).

7.2 Methanol: JT Baker Purge and Trap Grade (P/N 9077-02 or equivalent).

7.3 Toluene: Baker Resi-Analyzed, for Organic Residue Analysis (P/N 9336-02 or equivalent).

7.4 Benzene: Baker Resi-Analyzed, for Organic Residue Analysis (P/N 9256-2 or equivalent).

7.5 Sylon-CT: Supelco (P/N 3-3065 or equivalent). Sylon-CT is a highly reactive silonizing reagent consisting of 95% Toluene and 5% Dimethyldichlorosilane (DMDCS).

## 8 STANDARDS

8.1 Stock analytical standard solutions are purchased from Supelco Analytical. Other standards are prepared in the laboratory using neat compounds or prepared solutions purchased from Chemservice, AccuStandard, or other suppliers. Secondary dilutions are either made from purchased Supelco stock solutions are listed below or from prepared solutions as listed in the following:

| | | |
|---|---|---|
| Custom AC MIX 1 | 2000 ppm | 861213 |
| Custom AC MIX 2 | 2000 ppm | 861214 |
| Custom BN MIX1 | (VARIED) | 861212 |
| Custom BN MIX 2 | 2000 ppm | 861215 |
| BENZIDINE | 5000 ppm | 4-0005 |
| 3,3'-DICHLOROBENZIDINE | 5000 ppm | 4-0026 |
| N-NITROSODIPHENYLAMIN | 5000 ppm | 46702-U |
| OLMO4 SV MIX | 2000 ppm | 47514-U |
| 1,2,3-4 TCDD | 50 ppm | DD1234-50 (Protocol) |

8.1.1 Prepare 5ml working solutions at concentrations indicated in Table 4. Prepare by combining the indicated volumes of each stock solution into a 5ml volumetric flask. Dilute to the volume marker with methylene chloride.

8.1.2 Surrogate standards: A 2000 ppm Acid Surrogate standard is purchased from Supelco for use in preparing calibration standards and for spiking blanks, samples, and associated QA prior to extraction. A 2000-ppm BN Surrogate Standard is purchased from Supelco for use in the preparation of calibration standards and for spiking blanks, samples and associated QA prior to extraction.

| | |
| --- | --- |
| BN SURR | Supelco P/N 861252 |
| ACID SURR | Supelco P/N 861249 |

8.1.3 Internal Standards Solution: The Internal Standards Solution at 2000ppm is purchased from Supelco (P/N 861238) :

| | | |
| --- | --- | --- |
| 1,4-Dichlorobenzene-d4 | Naphthalene-d8 | Acenaphthene-d10 |
| Phenanthrene-d10 | Chrysene-d12 | Perylene-d12 |

8.1.4 The Internal Standard solution is stored in 10ml amber screw cap bottles with Teflon liners in the dark at 4oC. The Internal Standard solution is used in preparing all analytical standards. 20ul of this solution (2000ppm) per ml of sample extract is injected prior to analysis resulting in a concentration of 40ppm (ug/ml) in the extract.

8.1.5 A 1000-ppm tuning standard containing DFTPP, Pentachlorophenol and Benzidine is purchased from Supelco (P/N 46700-U. Prepare a 25 ppm standard by spiking 250 ul of the 1000 ppm standard into 9.75ml of Methylene Chloride

8.1.6 Information on prepared standard solution must be recorded in a standards logbook. Information such as standard supplier, lot

number, original concentration, a description of how the standard was made, are required along with the laboratory lot number, analyst's initials, date prepared, and verification signature. Standards must be remade every 12 months, or sooner, if the standards begin to show signs of unacceptable degradation. Class "A" volumetric must be used at all times and syringes, preferably gas-tight syringes when available, should be checked for accuracy using an analytical balance. Class "A" pipettes should also be used if volumes permit.

## 9 PRESERVATION AND HANDLING

9.1 All samples must be stored at 4°C upon receipt.

9.2 All samples must be extracted within 7 days of collection time.

9.3 All extracts must be analyzed within 40 days of extraction.

## 10 CALIBRATION

10.1 Instrument Calibration

10.1.1 Prior to calibration or sample analysis always verify that the analyzer is under sufficient vacuum and that the column has proper carrier gas flow.

10.1.2 Recommended GC/MS Operating Conditions:

| |
| --- |
| Mass Range: 35 to 500amu |
| Scan Time: 1 sec/scan |
| Initial Column Temperature and Hold Time: 45°C for 0.7 minutes |
| Column Temperature Program: 13°/min to 270, 30°/min to 310 |
| Final Column Temperature Hold: 300°C for 9 minutes |
| Injector Temperature: 275°C |

| |
|---|
| Transfer Line Temperature: 300°C |
| Source Temperature: Preset by H.P. at 280°C |
| Injector: Grob-type, splitless |
| Injection Volume: 1ul |
| Carrier Gas: Ultra High Purity Grade Helium at 30cm/sec. |
| Scan start time: 2.50 minutes |
| Splitless Valve Time: 0.75 minutes |

10.1.3 These conditions are used for all analytical standards for calibration and for all sample extracts to be analyzed following this method. For analysis of the DFTPP standard, 2ul is injected.

10.1.4 The column conditions, scan start time, and splitless valve time for analysis of DFTPP are as follows:

| |
|---|
| Initial Column Temperature and Hold Time: 140°C for 1 minute |
| Column Temperature Program: 140° to 300°C at 20°C/minute |
| Final Column Temperature Hold: 300C for 4minutes |
| Scan Start Time: approx. 5 minutes |
| Splitless Valve Time: 0.75 minutes |

10.2 Preparation of the Injection Port Liner and Installation Procedure.

Prior to the start of initial calibration and each daily analysis of sample extracts, a new liner for the injection port must be prepared. Once a liner has been used it is no longer inert and will cause serious chromatography problems with phenols and other compounds.

10.2.1 Remove one liner from a 40ml VOA bottle containing other liners immersed in Sylon-Ct solution. Rinse off the liner with Toluene and wipe dry. Insert partially into one end of the liner approximately 1cm of pre-silonized glass wool and trim neatly. Push the glass wool into the center of the liner so that it is 1 1/4" from the bottom. Do not use glass wool or solvents that

are dirty (i.e. suspended particles) or use liners which are chipped on the ends, deformed or fractured. Inspect the glass wool for cleanliness after it has been inserted. Using a Pasteur pipette flush out the interior of the liner containing the glass wool with Sylon-Ct. Rest the liner horizontally on a small beaker and allow the Sylon-Ct to re-deactivate the interior surfaces and the glass wool. There should be no air bubbles caught in the glass wool. After several minutes flush out the Sylon-Ct with toluene and finally with methanol. Dry the outer surface of the liner and rest it on the injection port housing until the remaining methanol is boiled off.

10.2.2 Insert the liner with the newly silonized glass wool plug into the injection port. Verify that the column extends up into the injection port and is perpendicular. Inspect the graphite seal and replace it if the edges are knife-shaped. The septum is always replaced daily. Bake out the column at 300°C for 15 minutes after the vacuum in the analyzer has returned to normal.

10.2.3 When preparing the liner, proper laboratory protection must be worn and the liner must be prepared in a well-ventilated hood. When the procedure is completed all traces of toluene, Sylon-Ct and methanol will be removed immediately so that extraction solvents and preparation of sample extracts will not come into contact with these solvents and become contaminated.

10.3 Tune the GC/MS system to meet the criteria listed in Sec. 12.1.1 by analyzing the DFTPP mix prepared in Sec. 8.1.5. After 50ng of DFTPP has been injected, analyzed and criteria met, then the analyzer parameters are satisfactory. These parameter settings are stored in a tune file, which will be used in all subsequent analysis of standards and sample extracts until the criteria fail, at which point the analyzer will have to be retuned and recalibrated.

10.4 CALIBRATION: Analyze the BNA Standard solutions prepared in Section 8.1 according to the conditions specified in Section 10.1.2.

Column performance and inertness of the injection port liner should be evaluated prior to analyzing these standards.

10.5 After the standards have been run, tabulate the area response of the characteristic ions listed in Table 1, against the concentration of each compound and its assigned internal standard (Refer to Table 2) and relative response factors (RRF) and % RSDs for each compound. Once the calibration range has been constructed, verify that the % RSD of the RF's is <35%. If all of the compounds meet these criteria, the system can be assumed linear & sample analysis may begin. The average RF from the initial calibration range is used to quantitate all samples.

10.6 Every 24 hours prior to analyzing sample extracts, and after DFTPP has been run and has met the tuning criteria, a check of the calibration range must be performed using the 50ppm check standard. Note that the compounds must have a % difference no greater than 20%. Corrective action must be taken to eliminate any problem with compounds that do not meet these criteria. If the problem cannot be resolved, after preparing another liner or clipping some of the column on the injection port side, for example, then another 5 point calibration range must be analyzed. Sample extracts may not be run until this action is taken.

11 PROCEDURE:

Sample Analysis

11.1 The GC/MS operator, prior to starting sample analysis, will generate a sequence program containing the list of the sample extracts to be analyzed, the position on the autosampler tray, and the proper acquisition and tune methods that are to be used. This sequence program contains all the necessary information on the samples to be analyzed and how the GC/MS system is to analyze them. The sample extracts are loaded onto the autosampler tray. Their position is verified by checking them against the ALS number on the sequence. This batch analysis will be performed automatically over the 24-hour period.

11.2 Data review, Interpretation, and Reporting

11.2.1 Data Review

11.2.1.1 After the sample extracts have been analyzed, the GC/MS operator will evaluate the sample results using Target to determine if the samples meet the criteria specified in Sec 15. For example, the analyst must determine that the sample was injected properly (through correct area counts of the internal standard quantitation ions) and that the surrogate recoveries are within limits. After determining that the analysis for the sample extract was satisfactory, the GC/MS operator will delete false positive hits. The operator will keep all positive (true) hits with the correct retention time. All surrogate, matrix spike, and other compound values will be checked for proper integration.

11.2.2 Interpretation

11.2.2.1 The operator shall examine the printed chromatogram for any irregularities such as filament shut-down, large peaks which did not fall into the compound retention window and thus were not integrated, and will note any other peaks which are unknown and may require library identification. The operator shall review and compare all sample target spectra with the corresponding standard target spectra. To qualify a target compound found in the analysis, the operator who reviews the data and interprets it must follow the guidelines listed below:

11.2.2.2 The most abundant ion in the standard target spectrum that equals 100% MUST also be present in the sample target spectrum. All other ions that are greater than

10% in the standard target spectra should also be present in the sample.

11.2.2.3 Sample target ions should agree to within ±20% of the abundance of those same ions in the standard target spectra.

11.2.2.4 If a library search is also performed on the sample extract to identify tentative compounds not associated with the calibration standards, the mass spectral interpreter shall use the guidelines above. In addition the interpreter shall note if the molecular ion is present in both the sample and reference spectra. If additional ions are present in the sample spectra the interpreter should determine if this is due to background contamination or the presence of coeluting compounds.

11.3 Reporting

11.3.1 The report consists of a two-page section of the total ion chromatogram and the remainder of the report is a page for each target compound found with a comparison of its spectra to the standard target spectra. The calculations of the concentrations of each target compound, in the original volume of the sample are reported in units of ppb (ug/l). Included with the reports is a copy of the laboratory extraction blanks that were extracted along with the samples. The client will also receive a copy of the calibration range, and copies of all check standard and tune standard reports necessary to complete the analysis. The client will receive a Tentatively Identified Compounds (TIC) report if requested. Finally the client will receive the Quality Assurance (QA) data associated with the batch the samples are in.

12 QUALITY CONTROL

12.1 GC/MS Tuning (DFTPP)

12.1.1 Prior to the analysis of any calibration standards or samples, the GC/MS system must meet all DFTPP key ion abundance criteria listed for a 50ng injection through the GC injection port.

| DFTPP Key Ions and Abundance Criteria** | |
| --- | --- |
| Mass | Ion Abundance Criteria |
| 51 | 30-60% of mass 198 |
| 68 | <2% of mass 69 |
| 69 | reference only |
| 70 | <2% of moss 69 |
| 127 | 40-60% of mass 198 |
| 197 | <1% of mass 198 |
| 198 | Base Peak, 100% relative abundance |
| 199 | 5-9% of mass 198 |
| 275 | 10-30% of mass 198 |
| 365 | >1% of mass 198 |
| 411 | 0-100% of mass 443 |
| 442 | >40% of mass 198 |
| 433 | 17-23% of mass 442 |

**These ion abundance criteria must be evaluated and meet criteria every 24 hours of sample analysis.

12.2 Method Blank

12.2.1 Method blanks are extracted with every sample batch on each day that samples are extracted. To be considered acceptable, the method blank must contain less than the MDL of all target compounds except for phthalates, which can be up to 5x's the MDL.

12.2.2 If a method blank does not meet these criteria, all affected samples must be re-extracted (volume permitting). Corrective

action must be taken to determine and eliminate the source of contamination

12.2.3 Surrogate recoveries for the method blank must be within the laboratory generated limits. If any surrogate is outside the limits, the method blank must re-analyzed. If any surrogate is still outside limits, all samples and QC samples associated with that method blank must be re-extracted (volume permitting).

12.3 Matrix Spike, Matrix Spike Duplicate and Spike Blank (LCS)

12.3.1 The QC spiked sample analyses and blank spike must be batched for water matrices. The frequency of these spiked analyses is a minimum of 1 per 20 samples, not to exceed 14 calendar days.

12.3.2 Matrix spike and blank spike percent recoveries are calculated and compared to the the limits specified in EPA 40 CFR, Part 136, Appendix A, Method 625, Table 6.

13. CALCULATIONS

13.1 See "SOP for Organic Calculations", SOP # OC04.

14. METHOD PERFORMANCE

14.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 3-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

14.2 All MDL results are available on file.

## 15. WASTE MANAGEMENT AND POLLUTION PREVENTION

### 15.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

### 15.2 POLLUTION PREVENTION:

15.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

15.2.2 The quantity of chemical purchased should be based on e expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

## 16. DATA ASSESMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1. Technical acceptance criteria for sample analysis

16.1.1. The samples must analyzed on a GC/MS system meeting the tune, initial calibration, continuing calibration and blank acceptance criteria.

16.1.2. The samples must be analyzed within 40 days of extraction date.

16.1.3. The samples must have an associated method blank which meets the technical acceptance criteria.

16.1.4. The % recovery of all surrogates must be within laboratory generated limits. See Table 3.

16.1.5. The RT of each ISTD must be within $\pm$ 30 seconds between the sample and the most recent continuing calibration standard.

16.1.6. The EICP area of each ISTD in the sample must be within +100, -50% from the most recent continuing calibration standard.

16.1.7. The elution of sample components should have the same RRT (relative retention time) as the components in the continuing calibration standard within 0.06 RRT units.

16.2. Corrective Action for Sample Analysis

16.2.1. Samples which have surrogates outside QC limits must be re-analyzed. If the recoveries are still outside QC limits, the sample must be re-extracted and analyzed, volume permitting. See Table 4 for surrogate limits.

16.2.2. If any ISTD does not meet the acceptance criteria for EICP area, the sample must be re-analyzed to confirm if a matrix effect exists.

16.2.3. Any sample extract containing a hit for a target compound that exceeds the calibration range must be diluted and re-analyzed.

16.3 Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

## 17. REFERENCES

17.1 EPA 40CFR, Part 136, Appendix A, Method 625

**TABLE 1**
**CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS**

| Compound | Primary Ion | Secondary Ion(s) |
|---|---|---|
| Acenaphthene | 154 | 153, 152 |
| Acenaphthylene | 152 | 151, 153 |
| Anthracene | 178 | 176, 179 |
| Benzidine | 184 | 92, 185 |
| Benzo(a)anthracene | 228 | 229, 226 |
| Benzo(b)fluoranthene | 252 | 253, 125 |
| Benzo(k)fluoranthene | 252 | 253, 125 |
| Benzo(g,h,i)perylene | 276 | 138, 277 |
| Benzo(a)pyrene | 252 | 253, 125 |
| Bis(2-chloroethoxy)methane | 93 | 95, 123 |
| Bis(2-chloroethyl)ether | 93 | 63, 95 |
| Bis(2-chloroisopropyl)ether | 45 | 77, 121 |
| Bis(2-ethylhexyl)phthalate | 149 | 167, 279 |
| 4-Bromophenyl phenyl ether | 248 | 250, 141 |
| Butyl benzyl phthalate | 149 | 91, 206 |
| 2-Chloronaphthalene | 107 | 144, 142 |
| 2-Chlorophenol | 128 | 64, 130 |
| 4-Chlorophenyl phenyl ether | 204 | 206, 141 |
| Chrysene | 228 | 226, 229 |
| Dibenz(a,h)anthracene | 278 | 139, 279 |
| Di-n-butylphthalate | 149 | 150, 104 |
| 1,3-Dichlorobenzene | 146 | 148, 111 |
| 1,4-Dichlorobenzene | 146 | 148, 111 |
| 1,2-Dichlorobenzene | 146 | 148, 111 |
| 3,3'-Dichlorobenzidine | 252 | 254, 126 |
| 2,4-Dichlorophenol | 162 | 164, 98 |
| Diethylphthalate | 149 | 177, 150 |
| 2,4-Dimethylphenol | 122 | 107, 121 |
| Dimethylphthalate | 163 | 194, 164 |
| 4,6-Dinitro-2-methylphenol | 198 | 51, 105 |
| 2,4-Dinitrophenol | 184 | 63, 154 |
| 2,4-Dinitrotoluene | 165 | 63, 89 |
| 2,6-Dinitrotoluene | 165 | 63, 89 |

**TABLE 1**
**CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS**

| Compound | Primary Ion | Secondary Ion(s) |
|---|---|---|
| 1,2-Diphenylhydrazine | 77 | 105, 182 |
| Di-n-octylphthalate | 149 | 167, 43 |
| Fluoranthene | 202 | 101, 203 |
| Fluorene | 166 | 165, 167 |
| 2-Fluorobiphenyl (surr.) | 172 | 171 |
| 2-Fluorophenol (surr.) | 112 | 64 |
| Hexachlorobenzene | 284 | 142, 249 |
| Hexachlorobutadiene | 225 | 223, 227 |
| Hexachlorocyclopentadiene | 237 | 235, 272 |
| Hexachloroethane | 117 | 201, 199 |
| Indeno(1,2,3-cd)pyrene | 276 | 138, 227 |
| Isophorone | 82 | 95,138 |
| Naphthalene | 128 | 129, 127 |
| Nitrobenzene | 77 | 123, 65 |
| Nitrobenzene-$d_5$ (surr.) | 82 | 128, 54 |
| 2-Nitrophenol | 139 | 109, 65 |
| 4-Nitrophenol | 139 | 109, 65 |
| N-Nitrosodimethylamine | 42 | 74, 44 |
| N-Nitrosodiphenylamine | 169 | 168, 167 |
| N-Nitrosodipropylamine | 70 | 42,101,130 |
| Pentachlorophenol | 266 | 264, 268 |
| Phenanthrene | 178 | 179, 176 |
| Phenol | 94 | 65, 66 |
| Phenol-$d_5$ (surr.) | 99 | 42, 71 |
| Pyrene | 202 | 200, 203 |
| Terphenyl-$d_{14}$ (surr.) | 244 | 122, 212 |
| 2,4,6-Tribromophenol (surr.) | 330 | 332, 141 |
| 1,2,4-Trichlorobenzene | 180 | 182, 145 |
| 2,4,6-Trichlorophenol | 196 | 198, 200 |

## TABLE 2
## SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

| 1,4-Dichlorobenzene-$d_4$ | Naphthalene-$d_8$ | Acenaphthene-$d_{10}$ |
|---|---|---|
| Bis(2-chloroethyl)ether | Bis(2-chloroethoxy)methane | Acenaphthene |
| Bis(2-chloroisopropyl)ether | 4-Chloro-3-methylphenol | Acenaphthylene |
| 2-Chlorophenol | 2,4-Dichlorophenol | 2-Chloronaphthalene |
| 1,3-Dichlorobenzene | 2,4-Dimethylphenol | 4-Chlorophenylphenylether |
| 1,4-Dichlorobenzene | Hexachlorobutadiene | Diethylphthalate |
| 1,2-Dichlorobenzene | Isophorone | Dimethylphthalate |
| 2-Fluorophenol (surr.) | Naphthalene | 2,4-Dinitrophenol |
| Hexachloroethane | Nitrobenzene | 2,4-Dinitrotoluene |
| N-Nitrosodimethylamine | Nitrobenzene-$d_5$ (surr.) | 2,6-Dinitrotoluene |
| N-Nitroso-di-n-propylamine | 2-Nitrophenol | Fluorene |
| Phenol | 1,2,4-Trichlorobenzene | 2-Fluorobiphenyl (surr.) |
| Phenol-$d_5$ (surr.) | | Hexachlorocyclopentadiene |
| | | 4-Nitrophenol |
| | | 2,4,6-Tribromophenol (surr.) |
| | | 2,4,6-Trichlorophenol |

**TABLE 2 (cont.)**
**SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION**

| Phenanthrene-$d_{10}$ | Chrysene-$d_{12}$ | Perylene-$d_{12}$ |
| --- | --- | --- |
| Anthracene | Benzo(a)anthracene | Benzo(b)fluoranthene |
| Benzidine | Bis(2-ethylhexyl)phthalate | Benzo(k)fluroanthene |
| 4-Bromophenylphenylether | Butylbenzylphthalate | Benzo(ghi)perylene |
| Di-n-butyl phthalate | Chrysene | Benzo(a)pyrene |
| 4,6-Dinitro-2-methylphenol | Pyrene | Dibenz(a,h)anthracene |
| 1,2-Diphenylhydrazine | Terphenyl-d14(surr.) | Di-n-octylphthalate |
| Fluoranthene | | Indeno(1,2,3-cd)pyrene |
| 3,3-Dichlorobenzidine | | |
| Hexachlorobenzene | | |
| N-Nitrosodiphenylamine | | |
| Pentachlorophenol | | |
| Phenanthrene | | |
| Benzidine | | |

**TABLE 3**

**LABORATORY GENERATED SURROGATE LIMITS**
**(updated annually)**

| ACID SURR | LIMITS | BN SUR | LIMITS |
| --- | --- | --- | --- |
| | | | |
| 2-Fluorophenol | 7-86 | Nitrobenzene-d5 | 35-136 |
| Phenol-d5 | 2-63 | 2-Flourobiphenyl | 33-135 |
| 2,4,6-Tribromophenol | 49-127 | Terphenyl-d14 | 25-174 |

**Table4**
**Working Standards Preparation**

| Solution No. | 5PPM | 10 PPM | 20 PPM | 50 PPM | 80 PPM | 120PPM |
|---|---|---|---|---|---|---|
| BN MIX1 | 50uL | - | - | - | - | - |
| BN MIX 2 | - | 25uL | 50uL | 250uL | 200uL | 300uL |
| 3,3-DCB | 10uL | 20uL | 50uL | 160uL | 100uL | 120uL |
| BENZIDINE | 20uL | 20uL | 50uL | 160uL | 200uL | 120uL |
| N-NITROSO. | 5uL | 10uL | 20uL | 100uL | 80uL | 120uL |
| CLP SV MIX | 12.5uL | 25uL | 50uL | 250uL | 200uL | 300uL |
| AC MIX 1 | 50uL | 50uL | 125uL | 400uL | 250uL | 300uL |
| AC MIX 2 | 12.5uL | 25uL | 50uL | 250uL | 200uL | 300uL |
| 1,2,3,4-TCDD | - | - | - | 100uL | - | - |
| ISTD | 100uL | 100uL | 100uL | 200uL | 100uL | 100uL |
| AC SURR | 12.5uL | 25uL | 50uL | 250uL | 200uL | 300uL |
| BN SURR | 12.5uL | 25uL | 50uL | 250uL | 200uL | 300uL |
| **FINAL VOLUME** | **5ML** | **5ML** | **5ML** | **10ML** | **5ML** | **5ML** |

**Table 5**
**QA Limits**

| Compound | Limits |
|---|---|
| Bis(2-Chloroethyl)ether | 12-158 |
| 1,3-Dichlorobenzene | 0-172 |
| 1,4-Dichlorobenzene | 20-124 |
| 1,2-Dichlorobenzene | 32-129 |
| Bis(2-Chloroisopropyl)ether | 36-166 |
| N-Nitroso-di-n-propylamine | 0-230 |
| Hexachloroethane | 40-113 |
| Nitrobenzene | 35-180 |
| Isophorone | 21-196 |
| Bis(2-Chloroethoxy)methane | 33-184 |
| 1,2,4-Trichlorobenzene | 44-142 |
| Naphthalene | 21-133 |
| Hexachlorobutadiene | 24-116 |
| 2-Chloronaphthalene | 60-118 |
| Dimethylphthalate | 0-112 |
| Acenaphthylene | 33-145 |
| 2,6-Dinitrotoluene | 50-158 |
| Acenaphthene | 47-145 |
| 2,4-Dinitrotoluene | 39-139 |
| Diethylphthalate | 0-114 |
| 4-Chlorophenyl-phenylether | 25-158 |
| Fluorene | 59-121 |
| 4-Bromophenyl-phenylether | 53-127 |
| Hexachlorobenzene | 0-152 |
| Phenanthrene | 54-120 |
| Anthracene | 27-133 |
| Di-n-butylphthalate | 01-118 |
| Fluoranthene | 26-137 |

**Table 5**
**QA Limits**
**(cont.)**

| Compound | Limits |
|---|---|
| Pyrene | 52-115 |
| Butylbenzylphthalate | 0-152 |
| 3,3'-Dichlorobenzidine | 0-262 |
| Benzo(a)anthracene | 33-143 |
| Chrysene | 17-168 |
| Bis(2-Ethylhexyl)phthalate | 08-158 |
| Di-n-octylphthalate | 04-146 |
| Benzo(b)fluoranthene | 24-159 |
| Benzo(k)fluoranthene | 11-162 |
| Benzo(a)pyrene | 17-163 |
| Ideno(1,2,3-cd)pyrene | 0-171 |
| Dibenz(a,h)anthracene | 0-227 |
| Benzo(g,h,i)perylene | 0-219 |
| | |

STL Edison Standard Operating Procedure

Title: SW8081A - Analysis of Organochlorine Pesticides by Gas Chromatography

Laboratory Director: _____

Technical Director: _____

QA Manager: _____

Department Manager: Catherine R. Balanga

File Location: F:\QAQC\SOPs\NELAC\NELAC SOPs 2004\120PEPCB\SW846\8081A04.DOC

Revision Date: 04/06/04

SOP Number 8081A04

REV 4



1. SCOPE AND APPLICATION



1.1. The general principles of Method 8081A can be applied to any gas chromatographic system. The procedure covers all aspects of normal daily activities for GC operation used for the analysis of the following organochlorine pesticides in extracts from solid and liquid matrices, using fused silica, open tubular, capillary columns with electron capture detectors (ECD).

| Compound Name : | CAS Registry No |
|---|---|
| Aldrin | 309-00-2 |
| ∝-BHC | 319-84-6 |
| β-BHC | 319-85-7 |
| γ-BHC (Lindane) | 58-89-9 |
| δ-BHC | 319-86-8 |
| Chlordane - (N.O.S.) | 57-74-9 |
| 4,4'-DDD | 72-54-8 |
| 4,4'-DDE | 72-55-9 |
| 4,4'-DDT | 50-29-3 |
| Dieldrin | 60-57-1 |
| Endosulfan I | 959-98-8 |
| Endosulfan II | 33213-65-9 |
| Endosulfan sulfate | 1031-07-8 |
| Endrin | 72-20-8 |
| Endrin Aldehyde | 7421-93-4 |
| Endrin Ketone | 53494-70-5 |
| Heptachlor | 76-44-8 |
| Heptachlor Epoxide | 1024-57-3 |
| Methoxychlor | 72-43-5 |
| Toxaphene | 8001-35-2 |

1.2. This procedure specifically addresses quantitative and confirmatory analysis of organochlorine pesticides using Agilent Technologies brand equipment. The samples analyzed are primarily environmental samples of soil, waste, water and leachate. This method covers all aspects of analysis

of organochlorine pesticides except for those aspects that pertain to extraction and clean up.

2. SUMMARY OF METHOD

2.1. A measured volume or weight of sample (15g for soil, 1 g for waste, 1000 ml for water, and 100 ml for TCLP) is extracted using the appropriate matrix-specific sample extraction technique. (The effective final volume is usually between 5 and 20 ml in hexane.)

2.2. Liquid samples are extracted at neutral pH with methylene chloride using either Method 3510C (separatory funnel) or Method 3520C (continuous liquid-liquid extractor).

2.3. Solid samples are extracted with hexane-acetone (1:1) using Method 3550B (ultrasonic extraction), or Method 3541 (automated soxhlet extraction). Both neat and diluted organic liquids (Method 3580A, Waste Dilution), may be analyzed by direct injection.

2.4. Extract cleanup steps are employed depending on the nature of the matrix interferences. Suggested cleanups include Florisil (Method 3620B) and TBA for sulfur (Method 3660B).

2.5. After cleanup, the extract is analyzed by injecting a 2-uL sample into an Agilent Technologies gas chromatograph equipped with a dual wide-bore fused silica capillary columns and electron capture detectors (GC/ECD).

2.6. For pesticide analysis a system performance check (DDT/Endrin breakdown) and a calibration verification standard must be run prior to analysis. Failure of either will generally indicate the need for injection port/column maintenance and/or recalibration.

2.7. Samples are analyzed after all the necessary checks have been performed. Samples analyzed for pesticides require an additional post analysis Quant Report to be printed and attached to the chromatographic report.

2.8. All samples are then manually reviewed. Secondary column confirmation of target compounds and quantitation are conducted by the analyst as required.

3. DEFINITIONS:

3.1. Refer to document DEFDOC-04 for definitions.

4. INTERFERENCES

4.1. Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

4.1.1. Interferences from phthalate esters can be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

4.2. The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Employ SW3660B for removal of sulfur. Endrin aldehyde recovery using the TBA procedure is drastically reduced. Accordingly, this compound must be determined prior to sulfur cleanup.

4.3. Co-eluting chlorophenols are eliminated by using SW3620B (Florisil).

4.4. Check Florisil prior to use to assure quantitative recovery of targeted analytes. Duplicate checks are required for each new lot or every three hundred samples whichever is more frequent.

4.4.1. Check Florisil by spiking 1ml of the Pest Mix midpoint and 0.5 ml of trichlorophenol onto the cartridge and concentrating to final volume of 1 ml. Inject 1 ul onto a capillary column, conducting the elution and analyzing the extract. Recovery is acceptable if all pesticides are recovered at 80 - 110%and the recovery of trichlorophenol is <5% and co-eluting interfering peaks are absent from the extract.

5. APPARATUS AND MATERIALS

5.1. Gas Chromatograph:

5.1.1. The system used is an HP and a Agilent Technologies (Avondale, PA) model 5890/6890 Gas Chromatograph (G.C.). It is equipped for simultaneous quantitation and confirmation columns using two separate detector channels on dual megabore capillary columns that are suitable for the analysis of organochlorine pesticides. All operations are as automated as possible with the equipment utilized.

5.1.2. Injection system: Sample injection is accomplished by a single auto injector. The auto injector is serviced by a robot arm that shuttles samples between the sample tray and the injector turret.

5.1.2.1. The samples are injected into a split/splitless injection port equipped with electronic pressure control (EPC). The injection port is normally operated in splitless mode during injection. The EPC is operated in the ramp flow mode.

5.1.2.2. Liners: The injection port is each fitted with replaceable, heavy-walled siltek-coated glass double gooseneck liner. The liner contains a plug of silanized glass wool approximately 1 cm in length. The glass wool is positioned in the liner between the double gooseneck. The liner is replaced on a regular maintenance schedule.

5.1.2.3. Oven and Columns: Temperature programmable gas chromatograph ovens are required, capable of integrated temperature control between 35°C and 350°C.

5.1.2.3.1. Two dissimilar columns are used for analysis. A Restek StxCLPesticides, 30m x 0.53mm ID x 0.5um film thickness column is used for sample quantitation. The secondary column is a Restek StxCLPesticides II, 30m x 0.53mm ID x 0.42um film thickness column.

5.1.2.4. Detectors: Sample detection is by electron capture. The G.C. is equipped with dual Electron Capture Detectors (ECD), one for each column.

5.1.2.4.1. Each detector is supplemented with make-up gas to provide sufficient detector flow for maintaining the electron plasma. This is in addition to the gas exiting the column. The make-up gas (P-5) is fed from a supply other than the injection port.

5.2. Data System:

5.2.1. The data system consists of Agilent Technologies GC Chemstation Revision A.09.01 and Agilent Technologies 3365 Series II DOS Chemstation Version A.03.01 1991 , which is used for acquisition and Target software (Thru-Put Systems) using a Falcon integrator for data processing.

6. REAGENTS

6.1. Gases: Ultra high purity (99.999%) Helium is used as the carrier and injection port purge gas. It is introduced to the GC at the injection port. Ultra high purity (99.999%) Argon (95%) / Methane (5%) (a.k.a. P-5 Mixture) is used as make-up gas. It is introduced to the GC via the make-up gas adapter at the end of the capillary column. They are supplied by M-G Industries (Valley Forge, PA). Both gases are supplied at tank pressures of 2000-2400 psig., for a 300 cft. tank. The tank pressure is regulated to an outlet pressure of 70 psig. Each tank is used until the tank pressure drops to less than 500 psig.

6.1.1. The gas streams are polished using three traps or filters before introduction to the G.C. The traps are as follows:

6.1.1.1. Hydrocarbon trap
6.1.1.2. $H_2O$ trap
6.1.1.3. $O_2$ scrubber

6.1.2. Both the moisture trap and the Oxygen scrubber are of the indicating type. They require either replacement or reconditioning upon color change of the active agents. Refer to the instructions for the individual traps to determine if it is still active. The hydrocarbon trap is a simple activated carbon trap. With high quality gas, it should last for an extended period of time (1-yr. minimum).

6.2. Solvents used in the extraction and cleanup procedures include n-hexane, diethyl ether, methylene chloride, and acetone that are exchanged to n-hexane prior to analysis.

6.3. Hexane is required in this procedure. All solvents must be pesticide quality or equivalent. Each lot of solvent is screened for contaminants before being used for analysis.

7. STANDARDS

7.1. Standards are purchased as a concentrated solution. The most common standard used is an 18 compound mixture of pesticides that is commonly referred to as Pest Mix. The components of Pest Mix are: alpha-BHC, beta-BHC, Lindane (gamma-BHC), delta-BHC, Endrin, Endrin Aldehyde, Endrin Ketone, Heptachlor, Heptachlor Epoxide, Aldrin, Dieldrin, Endosulfan I, II and Sulfate, Methoxychlor and 4,4'-DDD, DDE, DDT. The standard surrogates used are Tetrachloro-m-xylene (TCmX) and Decachlorobiphenyl (DCB).

NOTE: Two independent sources are used for quantitation standards and spiking standards

7.1.1. Most stock solutions are diluted (in volumetric glassware) to working concentration using hexane as the diluent.

7.2. Standard mixes and sources *.

| | |
| --- | --- |
| Supelpreme-HC (Pest Mix) | Supelco – 48913 |
| Pest Spike Mix | Supelco – 4S8913 second source |
| TCMX/DCB | Supelco – 48460 |
| TCMX/DCB Spike Mix | Supelco – 861275 |
| Endrin/DDT | Supelco – 48282 |
| Chlordane | Supelco – 48065U |
| Toxaphene | Supelco – 48103 |

*Suppliers with equivalent standards are also used.

7.2.1. Solution Preparation

7.2.1.1. Pest Mix (Calibration)

7.2.1.1.1. 500 ppb solution (200ppb DCB/TCMX):
7.2.1.1.2. 50ul of 2ug/ul Pest Mix, Dilute to 200ml
7.2.1.1.3. 200ul of .2ug/ul TCMX/DCB, Dilute to 200ml

7.2.1.1.4. 250 ppb solution (150ppb DCB/TCMX):
7.2.1.1.5. 25ul of 2ug/ul Pest Mix, Dilute to 200ml
7.2.1.1.6. 150ul of .2ug/ul TCMX/DCB, Dilute to 200ml

7.2.1.1.7. 100 ppb solution (100ppb DCB/TCMX):
7.2.1.1.8. 25ul of 2ug/ul Pest Mix, Dilute to 500ml
7.2.1.1.9. 250ul of .2ug/ul TCMX/DCB, Dilute to 500ml

7.2.1.1.10. 50 ppb solution (50ppb DCB/TCMX):
7.2.1.1.11. 6.25ul of 2ug/ul Pest Mix, Dilute to 250ml
7.2.1.1.12. 62.5ul of .2ug/ul TCMX/DCB, Dilute to 250ml

7.2.1.1.13. 10 ppb solution (25ppb DCB/TCMX):
7.2.1.1.14. 1.25ul of 2ug/ul Pest Mix, Dilute to 250ml
7.2.1.1.15. 31.25ul of .2ug/ul TCMX/DCB, Dilute to 250ml

7.2.1.2. Surrogate Spiking Solution
7.2.1.2.1. 10 ppm DCB & TCmX Mix Solution, custom blend in final volume of 50 ml (Acetone)

7.2.1.3. Surrogate Oil Spiking Solution
7.2.1.3.1. 0.5 ppm DCB &TCmX Oil Solution, 2.5 ml of 10 ug/ml solution, dilute to 50 ml (Acetone)

7.2.1.4. Pesticide Spiking Solution
7.2.1.4.1. 20 ppm Pest Mix Solution, 0.5 ml of 2000 ug/ml solution, Dilute to 50 ml (Acetone)

7.2.1.5. Pesticide Oil Spiking Solution
7.2.1.5.1. 2 ppm Pest Oil Mix Solution, 1 ml of 20 ug/ml solution, dilute to 10 ml (Acetone)

7.2.1.6. TCLP Pesticide Spiking Solution
7.2.1.6.1. 5 ppm Pest Mix 1, 25 ppm Chlor & 50 ppm Tox in Pest Mix 2, 0.05 ml of 2000 ug/ml Pest Mix 1 and 0.25 ml of 2000/4000, ug/ml Pest Mix 2, Dilute to 20 ml (Acetone)

7.2.1.7. System Performance Solution (Breakdown Check)

7.2.1.7.1. 125 ul of 500 ng/ul DDT/Endrin Mix, Dilute to 250 ml, Final Concentration = 250 ng/ml

7.2.1.8. Chlordane Calibration Solution (Surrogates: TCmX & DCB)

7.2.1.8.1. 1000 ppb solution; 100 ul of 1ug/ul chlordane stock; Surrogate, 100 ppb: 50 ul of 0.2 ug/ul;; Dilute to 100 ml in Hexane. NOTE: Midpoint calibration standard only for multiple responders.

7.2.1.9. Toxaphene Calibration Solution (Surrogates: TCmX & DCB)

7.2.1.9.1. 1000 ppb solution; 100 ul of 1ug/ul Toxaphene stock; Surrogate, 100 ppb: 50 ul of 0.2 ug/ul; Dilute to 100 ml in Hexane NOTE: Midpoint calibration standard only for multiple responders

8. PRESERVATION AND HANDLING

8.1. Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

8.2. Extract cleanup

8.2.1. Cleanup methods are dictated by the original sample matrix and the parameters being determined.

8.2.2. Cleanup of all water samples, if needed, is performed using Florisil and TBA sulfite. Blanks must also undergo cleanup following the same procedures as samples.

8.2.3. Cleanup of all soil samples is conducted using Florisil and, if needed, TBA sulfite. Blanks must also undergo cleanup following the same procedures as samples.

8.2.4. Check Florisil prior to use to assure quantitative recovery of target analytes. Duplicate checks are required for each new lot and every three hundred samples whichever is more frequent.

8.2.5. Check Florisil by spiking 1ml of the Pest Mix midpoint and 0.5 ml of trichlorophenol onto the cartridge and concentrating to final volume of 1 ml. Inject 1 ul onto a capillary column, conducting the elution and analyzing the extract. Recovery is acceptable if all pesticides are recovered at 80 - 110%and the recovery of trichlorophenol is <5% and co-eluting interfering peaks are absent from the extract.

9. SAFETY

9.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

9.2. The analyst must wear a protective lab coat, safety glasses, and gloves when handling all samples, extracts, standards and solvents.

9.3. All questions pertaining to any safety procedure should be brought to the department manager or STL Edison Safety Officer.

9.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

9.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Hexane | Flammable Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Methanol | Flammable Poison Irritant | 200 ppm-TWA | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| Methylene Chloride | Carcinogen Irritant | 25 ppm-TWA 125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 10. PROCEDURE

### 10.1. GAS CHROMATOGRAPH OPERATION

10.1.1. The sequence of events for G.C. analysis involves many steps. First the injection system and column performance and calibration must be verified. Maintenance operations are performed as needed. Then samples must be run on the instrument. Chromatograms and reports must be evaluated for content, integration and concentration. Re-runs and dilutions must be made based on the calibrations that were in effect at the time the sample was run. Lastly, a detailed analysis and calculations must be performed to determine the concentration of all the parameters for which the sample was analyzed.

10.1.2. <u>General Information</u>:

10.1.2.1. Injection System: A split/splitless injection port with electronic pressure control (EPC) is used. Thirty seconds after sample injection, the purge valve is turned on to facilitate the sweeping of any remaining residual solvent/sample from the injection port.

10.1.2.2. The EPC is used in the ramp flow mode. The ramp pressure program is as follows:

| Initial Pressure | InitialTime | Rate | Final Pressure | Hold |
|---|---|---|---|---|
| 12 psi | 2.5 min | 7 psi/min | 4 psi | 1.50 min |
| | | 5 psi/min | 9 psi | 1.40 min |
| | | 9 psi/min | 13 psi | 2.00 min |

10.1.2.3. For pesticide analysis the normal operating conditions of the injection port are as follows:

| | |
|---|---|
| Injection Temperature: | 250°C |
| Column flow: | 12.3 ml/minute |
| Split vent flow: | 60 ml/minute |
| EPC: | Pressure Ramp |

10.1.2.4. In addition to the EPC, the injection port is also equipped with a siltek-coated glass double goose neck liner that contains a 1 cm glass wool plug. The plug of glass wool is located in the liner between the double goose neck.

10.1.2.5. This liner/glass wool combination provides many functions. The glass wool serves as a heat sink rapidly vaporizing solvent and samples resulting in higher response factors. The liner also protects the column head from accumulation of high boiling residuals and particulates.

10.1.2.6. The glass wool will be changed when changing the liner. The changing of the glass wool/liner is based upon the breakdown of an Endrin/DDT standard. This is covered in further detail in section 10.2.1.

10.1.2.7. Regular maintenance is performed on the injection port. When the glass wool/liner is changed, the septa also must be changed. Injection port, oven and detector temperatures are lowered to ambient prior to "cracking" the system. This is so as to introduce a minimum of damaging oxygen molecules into the system.

10.1.2.8. After the system has cooled, the old liner is removed. The injection port should be checked for particulate residues and cleaned as needed. A flashlight is usually required for this. After a new liner has been prepared it is placed into the injection port. A graphite seal is placed around the liner. The edges of the seal must be flat, not knife-edged, and free of nicks or burrs. If any of these conditions are not met, the graphite seal must be replaced as well. The graphite seal is critical to proper operation of the injection port. If in doubt, replace it.

10.1.2.9. The locking ring on the top of the injection port should be turned, with the wrench, about 1/8 turn past finger tight. The septum nut should never be tightened more than finger tight. After the injection port is reassembled, all column nuts inside the oven should be checked for leaks using Snoop (Supelco) or another suitable leak tester.

10.1.2.10. Once the signal from both detectors has stabilized, it is time to re-heat the zones. The zones should be heated in the order of detectors, oven and then injectors. This is to ensure that volatilized contaminants do not condense on the column or detector.

10.1.2.11. Oven: With the megabore columns installed, temperature programming is employed to achieve higher resolution of compounds and shorter run times than could be accomplished using isothermal methods.

10.1.2.11.1. A standard oven program for pesticide analysis is employed for all columns as follows:

| Initial Temp | Hold Time1 | Rate1 | Temp1 |
|---|---|---|---|

| | | | |
|---|---|---|---|
| 160°C | 0.62 min | 30°/min | 244°C |

| Hold Time2 | Rate 2 | Final Temp | Final Time |
|---|---|---|---|
| 2.5min | 21°/min | 315°C | 3.0min |

10.1.2.12. Detectors: Detectors operate at 330°C and need to be supplied with 60 ml/min total flow. They are essentially maintenance free on a day-to-day basis. They are routinely baked out at 330°C to remove persistent contaminants. On occasion the detectors may be baked out at a higher temperature to remove contaminants with an extremely high boiling point (CAUTION: Do not exceed the maximum detector temperature of 380°C).

10.1.2.12.1. If the detectors are particularly contaminated, they must be sent to Agilent Technologies in Avondale, Pennsylvania for reconditioning. This should occur if the detector baseline is greater than 100 Hz. Detector reconditioning should be required at a maximum of biannually.

10.1.2.13. Chemstation: The Chemstation is responsible for automation of runs and acquisition. The system is dedicated to a single GC and does not multitask. Therefore, data manipulation cannot be done while sample analysis is in progress. The data system acquires and stores all chromatographic data.

10.1.2.14. Target: Target is responsible for the processing of the data files. Calibrations, verification standards and samples are processed and reviewed using this database. All reports are also generated by Target.

10.2. G.C. SYSTEM PERFORMANCE CHECK

10.2.1. Endrin/4,4'-DDT Breakdown:

10.2.1.1. Prior to performing any standards or sample analysis, a daily check is made on the chromatographic performance of the system. This performance check is made by injecting a standard of Endrin and DDT, each at a 250-ppb level, and calculating the percentage breakdown for each compound.

10.2.1.2. If the system is working perfectly, only two peaks will be seen (one for Endrin and one for DDT). As a rule, this is not the case. It is normal to observe up to six peaks. One peak each for Endrin and its degradation products Endrin Aldehyde (EA) and Endrin Ketone (EK) and three peaks total for DDT and its degradation products DDE and DDD. If the percentage breakdown for either Endrin or DDT is greater than 15%, the system CANNOT be used for pesticide analysis.

10.2.1.3. The percentage breakdown is calculated as follows:

Endrin

$$\frac{\text{(Area of EA + EK)}}{\text{(Area of EA + EK + Endrin)}} \times 100 = \%\ \text{breakdown}$$

DDT

$$\frac{\text{(Area of DDE + DDD)}}{\text{(Area of DDE + DDD + DDT)}} \times 100 = \%\ \text{breakdown}$$

10.2.1.4. If the Endrin/DDT performance check fails and pesticide samples need to be analyzed, then injection port/column maintenance must be performed. Usually, changing the glass wool/liner will cure most breakdown problems in the injection port. Depending upon the nature of the samples, the entire injection port will occasionally need to be cleaned. This cleaning is best done with 1:1 Acetone: Hexane.

10.2.1.5. The septa should be changed each time the injection port is opened. Another routine maintenance operation to improve column performance is the removal of the first 3 cm of the column.

10.2.1.6. After injection port/column maintenance has been performed, and the columns have been given time to equilibrate (baseline back down to normal) the Endrin/DDT must be re-injected and the system performance reevaluated.

10.3. EXTERNAL STANDARD CALIBRATION

10.3.1. Calibration Ranges:

10.3.1.1. Single component pesticides are calibrated using a five-point calibration range. Multi-component pesticides are calibrated using a single point calibration at the anticipated midpoint of the calibration range. Standards are prepared following the instructions in section 5.4.

10.3.1.2. The response factor, defined as the ratio of the area to the standard concentration, is calculated for each analyte at each calibration concentration. The average response factor (if the % RSD across the 5 point range is $<20\%$) or a linear calibration not through the origin (if the correlation coefficient (r1) is $\geq 0.99$) is used for quantitation. Calibration is checked every 12 hours or after every twenty (20) samples, whichever comes first, by injecting a calibration verification standard for all single component pesticide standards.

The standard five point calibration ranges are:
Pesticides: 10, 50, 100, 250 and 500 ppb
Surrogates: 25, 50, 100, 150, 200 ppb
Chlordane: 1000 ppb
Toxaphene: 1000 ppb

10.3.1.3. Single component Pesticide Calibration: Calibration is accomplished en masse. All eighteen single component pesticides and two surrogates are calibrated with the 5 concentrations of Pest Mix using the Target Chromatography System.

10.3.1.3.1. Generating a calibration table: After the five calibration standards have been run, the data

files are copied to the Target Chromatography System. A new Target batch is created and the method file from the previous Target batch is copied to the new Target batch.

10.3.1.4. The data files representing the five levels of calibration also copied to the new Target batch and processed with the method file. The integrations of the five levels are checked for consistency in Target Review.

10.3.1.4.1. Linear Calibration. Check the percent relative standard deviation (% RSD) of the response factors for each individual analyte. If the % RSD is less than 20% over its working range, the linearity of the range is assumed. The average value of the response factors is used for quantitation of all the samples and verification standards.

10.3.1.4.2. Linear Calibration Using Least Squares Regression. If the % RSD is >20% for any given compound, a first order linear regression can be applied to the data to calculate the calibration curve and determine sample concentration. If this method is employed, the $r^1$ (Correlation Coefficient) value must be $\geq$ 0.99 for the calibration to be acceptable.

10.3.1.4.3. Alternative Non-Linear Calibration. In those instances where the RSD for one or more analytes exceeds 20%, the initial calibration may still be acceptable if the following conditions are met:

10.3.1.4.3.1. The mean of the RSD values for <u>all</u> analytes in the calibration is less than or equal to 20%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of all analytes.

10.3.1.4.3.2. The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the target analyte is part

of the calibration standard, its RSD value is included in the evaluation.

10.3.1.4.3.3. A summary of the initial calibration data must be reported to the client with a list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation.

10.3.1.4.3.4. If all of the conditions in Sec. 9.3.1.4.3.1 are met, then the average calibration or response factor may be used to determine sample concentrations.

10.3.1.4.4. Chlordane and Toxaphene Calibration: Chlordane and Toxaphene are multiple response pesticides and are calibrated using three to eight peaks.

10.3.2. Calibration Verification:

10.3.2.1. After the initial calibration range has been run, a verification standard is run to verify the continued validity of the calibration range. This is required every 12 hour shift and is performed after the last sample analyzed within the 12 hour period. The verification standard is chosen as the middle concentration of a calibration range. The Pest Mix verification standards' concentrations are 100ppb each.

10.3.2.2. Pesticide Breakdown Check and Verification Standard: At the beginning of a sequence's run, before or after the Endrin/DDT breakdown check, a Pest Mix 100 ppb check standard is run. After the data is analyzed, a Continuing Calibration Custom Report is generated from the verification standard's data file using the most recent calibration range. The eighteen pesticides plus surrogates must be checked to determine that the actual concentration in the check standard must be within +/- 15% of the expected concentration. If any of the pesticides fall out of the acceptability limits, the other four concentrations of Pest Mix, which constitute the calibration range, must be run. A new calibration range must now be constructed.

10.3.2.3. At the end of the analysis sequence, a 100ppb Pest Mix standard is analyzed. This standard must meet the criteria for calibration verification. This is known as the closing standard.

10.3.2.4. Samples are always quantitated against the average response factor or calibration curve whichever is applicable. Calibration verification standards only check the validity of the calibration range. Calibration verification standards are never used to quantitate samples.

10.3.3. Retention Time Windows

10.3.3.1. Retention time windows must be established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. All gas chromatographs used for pesticides analysis are equipped with electronic pressure control (EPC). The use of EPC results in little retention time variability between analysis. Accordingly, retention time variability for the purpose of retention time window determination for standards analysis is extremely small. The default window option must therefore be employed as follows to accommodate the excellent precision of EPC equipped systems.

10.3.3.2. Obtain the retention time for all single component compounds from the analysis of the midpoint standard for the calibration curve.

10.3.3.3. Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

10.3.3.4. The absolute retention times of the calibration verification are also checked against the retention time

window established by the mid-point standard of the initial calibration.

10.3.3.5. Apply the retention time window data in table 1 to its corresponding compound.

10.3.3.6. Calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when whenever a chromatographic column is replaced or a new detector is installed.

10.3.3.7. Whenever the observed retention time of each analyte and surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

10.3.4. Sequence for Analysis

10.3.4.1. Setting Up for Analysis: The first operations to be performed when preparing for analysis are the calibration and performance checks.

10.3.4.2. Performance and Check Standards: The instrument must first run the Endrin/DDT breakdown standard. This is to evaluate the performance of the injection port and column with regard to catalytic active sites. The breakdown must be less than 15% for both Endrin and DDT. If not, the performance check fails.

10.3.4.3. The instrument calibration for the 18 single response pesticides plus surrogates must next be check. This is accomplished by running the Pest Mix 100 ppb check standard. The actual concentration for each pesticide must be +/- 15 % of the expected concentration. Alternatively, the average concentration of all pesticides in the check standard must be ≤15%. If this criteria cannot be achieved for all pesticides and surrogates, the check standard fails.

10.3.4.4. The breakdown standard Endrin/DDT is acquired and measured before samples are analyzed and at the beginning of each 12 hour shift. If the breakdown check fails, then injection port/column maintenance is required. If a calibration check standard fails, then recalibration is necessary.

NOTE: The 12 hour time clock for Pesticides commences with the injection of the first Pesticide Calibration Standard or Verification

10.3.4.5. Calibration for Non-Pest Mix Pesticides: The instrument may be calibrated for quantitation of any semi-volatile, organochlorine pesticide. The pesticides that are most commonly calibrated for and are not included in the Pest Mix are Chlordane and Toxaphene.

10.3.4.6. Chlordane and Toxaphene are multiple response pesticides containing at least 3-8 primary peaks each. Both pesticides use area vs. concentration to generate a single point calibration using Target. The single point calibration check standard concentration is 1000ug/l for Chlordane and Toxaphene. The multiple peak responders calibration check standard should be analyzed only if the Pest Mix calibration ranges are being acquired.

10.3.5. Analysis Sequence: The automation of G.C. runs is accomplished via the "SEQUENCE" macro of the Chemstation.

Idealized Analysis Sequence *

Endrin/DDT
Pest Mix 100 ppb Check Standard
Additional Pesticide Check Standards
Blanks and Spike Blanks
QA's (Sample, MS, MSD)
Rush Samples
Remaining Samples
Oil Samples

10.3.5.1. After 20 samples or12 hours of analysis, a Pesticide mix standard bracket must be analyzed. In order to continue with sample analysis these brackets must be within ± 15% of the expected concentrations.

10.3.5.2. The Sequence File: The sequence file contains the name of Method file corresponding to the type of analysis to be performed, the range of samples to be run, and the number of injections per bottle.

10.3.5.3. It is common practice to run the check standards, evaluate the instrument status, and then complete the Sample Table and Sequence File. If everything else is complete, the run is initiated using the START SEQUENCE soft-key of the SEQUENCE macro.

10.3.6. Pesticide Report Printing: As previously mentioned, the Target Chromatography System will calculate the concentrations of 18 single response pesticides surrogates.

10.4. DOCUMENTATION

10.4.1. Before the analysis sequence is initiated the GC Performance and Repairs logbook must be filled out. It should contain the following information: date, injector temp, oven temp, detector temp, column A flow, column B flow, signal A, signal B, analysts initials, and notes for any necessary repairs.

10.4.2. After samples have been run, each standard and sample must be entered into the Instrument Run Log. The Instrument Run Log should contain the following information: run date, data file name, vial position, sample number, initial volume/weight, final volume, dilution factor, method, job number, QA number, extraction date, lab prep batch, target batch signature of analyst at the bottom of each page, lot numbers for standards used, and result of run (O.K., dilution, non-inject, etc.).

11. QUALITY CONTROL

11.1. Matrix Spikes. On an ongoing basis a matrix spike, matrix spike duplicate and blank spike must be analyzed for every 20 environmental samples. If the spiked sample recovery results fall outside the laboratory generated

limits, the blank spike recovery is evaluated. If the blank spike recovery is within limits the poor sample recovery results are attributed for matrix interference. If the blank spike recovery results are outside QC limits, first the extract is reanalyzed and if it is still outside the limits the entire QA batch must be reextracted and reanalyzed.

11.2. Reagent Blanks. The analytical results for reagent blank analysis must fall below the reporting limit for each compound of interest. If a target compound is detected in the blank at a concentration higher than the reporting limit, first the extract is reanalyzed and if it is still outside the limits the entire batch of samples extracted with the affected blank must be reextracted.

11.3. Surrogate Standards. All samples, blanks and QA samples are spiked with a 2 component "surrogate" standard mix (TCmX & DCB). If both TCmX and DCB recovery is outside their acceptance ranges, the sample extract is reanalyzed. If the recovery is still outside the limits the sample must be reextracted and reanalyzed or the data flagged as "estimated concentration".

12. CALCULATIONS

See SOP#OC04 for Organic Calculations.

13. METHOD PERFORMANCE

13.1. A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2. All MDL results are available on file.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. POLLUTION PREVENTION:

14.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15. DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1. Technical acceptance criteria for sample analysis.

15.1.1. The samples must be analyzed on a GC system meeting the initial calibration, continuing calibration and blank technical acceptance criteria.

15.1.2. The sample must be analyzed within the required holding time.

15.1.3. The sample must have an associated method blank meeting the blank technical acceptance criteria.

15.1.4. The percent recovery of each of the system monitoring compounds in the sample must be within the acceptance windows.

15.1.5. The retention time shift for each of the internal standards must be within +/- 0.50 minutes (30 seconds) between the sample and the most recent continuing calibration standard analysis.

15.1.6. After analyzing a sample that exceeds the initial calibration range the analyst must either analyze an instrument blank (using the same purge inlet if using an auto sampler) which must meet technical acceptance criteria for blank analysis or monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If auto sampler is used, the next sample analyzed using the same purge inlet must also meet the maximum contamination criteria. If the maximum criteria is exceeded then all samples affected by the carryover must be re-analyzed.

15.2. Corrective Action for Sample Analysis

15.2.1. Samples must meet technical acceptance criteria before reporting data.

15.2.2. Corrective action for failure to meet instrument performance checks, initial, continuing calibration and method blanks must be completed prior to sample analysis.

15.2.3. Corrective action for system monitoring compounds and internal standard compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

15.2.4. If any of the system monitoring compounds and internal standard compounds fail to meet acceptance criteria:

- Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system

monitoring compound recoveries and internal standard compound responses meet acceptance criteria.

- If the instrument log for the amount of internal standard compound spiking solution which was added. If an incorrect amount was spiked reanalyze with the correct amount.
- Check the preparation of the internal standards and system monitoring compounds for concentration and expiration.
- Verify that the instrument is operation correctly.

15.2.5. Determine if the problem was a matrix effect.

15.2.6. Check the surrogate recoveries for the MS and MSD.

15.2.7. If the system monitoring compound recoveries and the internal standard compound recoveries meet the acceptance criteria in the reanalyzed samples the samples are considered in control and the data may be reported.

15.2.8. If the system monitoring compound recoveries and the internal standard compound responses do not meet the acceptance criteria in the reanalyzed samples, then submit data from both analyses.

## 16. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1. Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. Data qualifiers can be found in Appendix A. If applicable, a Corrective Action Reports will be initiated in order to provide for investigation and follow-up.

## 17. REFERENCES

17.1. United States Environmental Protection Agency, "Method SW8000B: Determinative Chromatographic Separations, Method 8081A Organochlorine Pesticide by Gas Chromatography", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 3, December 1996.

**Table 1**
**Retention Time (RT) Windows For Single Analytes/Surrogates**

| Compound | RT Window (minutes) |
|---|---|
| alpha-BHC | ±0.05 |
| beta-BHC | ±0.05 |
| gamma-BHC (Lindane) | ±0.05 |
| delta-BHC | ±0.05 |
| Heptachlor | ±0.05 |
| Aldrin | ±0.05 |
| alpha-Chlordane | ±0.07 |
| gamma-Chlordane | ±0.07 |
| Heptachlor Epoxide | ±0.07 |
| Dieldrin | ±0.07 |
| Endrin | ±0.07 |
| Endrin aldehyde | ±0.07 |
| Endrin Ketone | ±0.07 |
| 4,4'-DDD | ±0.07 |
| 4,4'-DDE | ±0.07 |
| 4,4'-DDT | ±0.07 |
| Endosulfan 1 | ±0.07 |
| Endosulfan 11 | ±0.07 |
| Endosulfan sulfate | ±0.07 |
| Methoxychlor | ±0.07 |
| Toxaphene | ±0.07 |
| Tetrachloro-m-xylene | ±0.05 |
| Decachlorobiphenyl | ±0.10 |

## Table 2

### Laboratory Generated Spike/RPD/Surrogate Limits (updated annually)

| Compound | SOX | | | | | |
|---|---|---|---|---|---|---|
| | aqueous | RPD | non-aqueous | RPD | Leachate | RPD |
| Aldrin | 59-155 | 12 | 53-140 | 18 | | |
| alpha-BHC | 66-122 | 12 | 49-147 | 19 | | |
| beta-BHC | 69-125 | 14 | 55-155 | 20 | | |
| delta-BHC | 72-124 | 12 | 51-144 | 16 | | |
| gamma-BHC(Lindane) | 65-124 | 11 | 51-141 | 18 | 72-177 | 19 |
| 4,4'-DDD | 84-143 | 14 | 70-152 | 21 | | |
| 4,4'-DDE | 71-141 | 15 | 41-172 | 22 | | |
| 4,4'-DDT | 85-133 | 17 | 62-155 | 46 | | |
| Dieldrin | 79-128 | 14 | 64-139 | 18 | | |
| Endosulfan I | 75-125 | 11 | 55-137 | 18 | | |
| Endosulfan II | 72-134 | 12 | 58-139 | 14 | | |
| Endosulfan sulfate | 67-143 | 15 | 55-142 | 18 | | |
| Endrin | 31-167 | 54 | 66-148 | 11 | 61-259 | 56 |
| Endrin aldehyde | 63-131 | 15 | 33-147 | 21 | | |
| Endrin ketone | 68-144 | 15 | 65-135 | 19 | | |
| Heptachlor | 66-113 | 11 | 57-142 | 19 | 86-214 | 22 |
| Heptachlor epoxide | 79-122 | 12 | 53-139 | 17 | 89-205 | 12 |
| Methoxychlor | 86-128 | 14 | 80-143 | 44 | 70-269 | 13 |
| Toxaphene | *70-130* | *40* | *70-130* | *40* | 58-201 | 17 |
| Chlordane | *70-130* | *40* | *70-130* | *40* | 82-193 | 12 |

| Surrogate | SOX | | |
|---|---|---|---|
| | aqueous | non-aqueous | Leachate |
| Tetrachloro-m-xylene | 50-124 | 52-148 | 68-123 |
| Decachlorobiphenyl | 33-141 | 48-169 | 60-156 |

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

# TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 1613B, 23, 0023A, and TO-9A

(SUPERSEDES: KNOX-ID-0004, Rev. 5)

Prepared By: _____ 9/28/05

Reviewed By: _____ 9/28/05
Technical Specialist

Approved By: _____ 09/28/05
Quality Assurance Manager

Approved By: _____ 9-28-05
Environmental, Health and Safety Coordinator

Approved By: _____ 9-28-05
Laboratory Director

Proprietary Information Statement:

This documentation has been prepared by Severn Trent Laboratories (STL) solely for STL's own use and the use of STL's customers in evaluating its qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to STL upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use if for any other purpose other than that for which it was specifically provided. The user also agrees that where consultants or other outside parties are involved in the evaluation process, access to these documents shall not be given to said parties unless those parties also specifically agree to these conditions.

## 1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 8290, 1613B, 23, 0023A, or TO-9A is specified.

1.2 The seventeen 2,3,7,8-substituted PCDDs/PCDFs listed in Table 1 may be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In addition, total homologs (i.e., Total TCDD, Total TCDF, etc.) may be identified by this method.

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be quantitated with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

## 2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 13 and Table 15. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged with hexane. The extract is then subjected to one or more cleanup steps to rid the sample of interferences. The final extract is prepared by adding a known amount of the labeled recovery standards (13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acid coextractables. If such interferences are not removed

before column chromatography, they may cause a shift in the predicted elution pattern. Conditions which may indicate the need for this procedure are: samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances. The identification of 2,3,7,8-TCDF is confirmed on an isomer specific (DB-225) GC column.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

## 3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 5 and Table 6.

3.4 Cleanup Standard: 37Cl4-2,3,7,8-TCDD which is added to samples, blanks, quality control samples, and calibration solutions. It is added to the samples after extraction but prior to extract cleanup, and is used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable

resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley < 25%).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 5 and Table 6.

3.8 Detection Limit (DL): The minimum concentration of the target analyte that can be detected. Sample specific detection limits are calculated from the instrument noise level and internal standard response.

3.9 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.10 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal in the same retention time region as a target analyte but which does not meet the other qualitative identification criteria defined in the procedure.

3.11 GC: Gas chromatograph or gas chromatography

3.12 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.13 HRGC: High resolution GC

3.14 HRMS: High resolution MS

3.15 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the initial calibration to verify the concentration of the Initial Calibration Standards.

3.16 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.17 IPR: Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

3.18 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.19 Laboratory Blank: See Method Blank.

3.20 Laboratory Control Sample: See Ongoing Precision and Recovery Standard (OPR).

3.21 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.22 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix, free of the targets of interest and interferences, that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.23 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.24 MS: Mass spectrometer or mass spectrometry.

3.25 Multiple Ion Detection (MID): A MS operational mode in which only selected ions are monitored rather than scanning the instrument to obtain a complete mass spectrum.

3.26 OPR: Ongoing precision and recovery standard; a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.27 PAR: Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.28 PCDD: Polychlorinated dibenzo-p-dioxins.

3.29 PCDF: Polychlorinated dibenzofurans.

3.30 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.31 Recovery Standard: 13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standard.

3.32 Relative Percent Difference (RPD): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.33 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples.

3.34 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.35 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.36 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

3.37 Additional definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.

## 4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2 The use of high purity reagents and solvents helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

## 5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile clean room gloves are worn. For operations using solvents that splash, silver shield gloves are recommended. Silver shield gloves protect against breakthrough for most of the solvents used in this procedure

5.3 Finely divided dry soils contaminated with PCDDs and PCDFs may be particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be processed in a confined environment, such as a hood or a glove box.

5.4 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.5 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.6 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source may be removed from the vacuum manifold through a vacuum interlock.

5.7 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument may be left on.

5.8 Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.9 When using a scalpel, cut away from yourself. If you are holding something, cut away from your hand.

5.10 Equipment goggles or a face shield must be used when employees are using solvents to rinse or clean glassware.

5.11 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Sulfuric Acid (1) | Corrosive, Oxidizer, Dehydradator | 1 mg/m$^3$ | This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system. |
| Sodium Hydroxide | Corrosive, Poison | 2 ppm, 5 mg/m$^3$ | This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system. |

| | | | |
|---|---|---|---|
| Hydrochloric Acid | Corrosive, Poison | 5 ppm-Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Methylene Chloride | Carcinogen, Irritant | 25 ppm-TWA, 125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| Hexane | Flammable, Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Methanol | Flammable, Poison, Irritant | 200 ppm-TWA | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| Toluene | Flammable, Poison, Irritant | 200 ppm-TWA<br>300 ppm-Ceiling | Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin. |
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Cyclohexane | Flammable, Irritant | 300 ppm TWA | Inhalation of vapors causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. High concentrations have a narcotic effect. |
| Tetradecane | Irritant | None established | Inhalation of vapors may cause difficulty breathing, headache, intoxication and central nervous system damage. |

| | | | |
|---|---|---|---|
| Benzene | Flammable, Toxic, Carcinogen | PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL | Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim may experience tightness in the chest, breathlessness, and loss of consciousness. |
| Nonane | Flammable | None established | Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation. |
| Potassium Hydroxide | Corrosive, Poison | 2 mg/m3 ceiling | Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on the severity of exposure. Symptoms may include coughing, sneezing, and damage to the nasal or respiratory tract. High concentrations can cause lung damage. Corrosive! Contact with skin can cause irritation or severe burns and scarring with greater exposures. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

5.11.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8- substituted PCDD or PCDF isomers.

**Note: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.**

5.12 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.13 The preparation of all standards and reagents and glassware cleaning procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.14 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

5.15 Training: Workers must complete the employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.16 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.17 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Benchtops should be covered with plastic backed absorbent paper.

5.18 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.19 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

## 6. Equipment and Supplies

6.1 Sample Extraction Equipment.

Note: All glassware used in extraction and cleanup procedures is solvent rinsed twice before use with acetone, toluene, methylene chloride and hexane in that order. Pre-extract the Soxhlet apparatus with toluene for at least 4 hours. Rinse glassware with all 4 solvents once. See SOP KNOX-QA-0002, current revision, "Glassware Cleaning", for details.

6.1.1 Aqueous Sample Extraction

6.1.1.1 Multi-position separatory funnel rotator.

6.1.1.2 2000 mL separatory funnels with PFTE stopcocks and PFTE stoppers.

6.1.1.3 100 mm glass funnels with short stems.

6.1.1.4 Class A 1 mL pipettes.

6.1.1.5 1000 mL graduated cylinders.

6.1.1.6 PFTE squirt bottles, 500 mL.

6.1.1.7 Syringes.

6.1.1.8 Glass wool, precleaned with methylene chloride.

6.1.1.9 Buchner funnels, filter flasks, rubber stopper and GF/D filters

6.1.1.10 Vacuum source

6.1.2 Soxhlet Extraction

6.1.2.1 Analytical balance, capable of weighing to 0.01 g.

6.1.2.2 Stainless steel spatula.

6.1.2.3 Stainless steel tweezers.

6.1.2.4 Soxhlet extractor or Dean-Stark Soxhlet extractor.

6.1.2.5 Heating mantles with temperature controls.

6.1.2.6 500 mL evaporative flask, round bottom.

6.1.2.7 Glass condenser, compatible with the dean-stark extractor.

6.1.2.8 Class A 1 mL pipettes.

6.1.2.9 Glass wool, precleaned with methylene chloride.

6.1.2.10 High purity glass fiber Soxhlet thimble.

6.1.2.11 Boiling beads, 6 mm glass.

6.1.2.12 PFTE boiling chips.

6.1.3 Waste Dilution

6.1.3.1 Analytical balance, capable of weighing to 0.01 g.

6.1.3.2 40 mL vial, with PFTE lined cap.

6.1.3.3 5 3/4 inch borosilicate glass pipets.

6.1.3.4 Rubber bulbs.

6.1.3.5 1 ml Class A pipette.

6.2 Sample Cleanup Equipment.

6.2.1 Acid-base cleanup

6.2.1.1 Disposable Pasteur pipets and rubber bulbs.

6.2.1.2 Graduated cylinder, 100 mL volume.

6.2.1.3 Vials, 40 mL volume, with PFTE lined caps.

6.2.2 Dual column cleanup

6.2.2.1 Disposable glass columns.

6.2.2.1.1 20mm x 240mm custom glass column with support ring and tapered tip.

6.2.2.1.2 16mm x 240mm custom glass column with support ring and tapered tip.

6.2.2.2 Aluminum support rack for custom columns.

6.2.2.3 Amber-colored glass jar with a PFTE lined screw cap, 250mL.

6.2.2.4 Volumetric flask, 100 mL volume.

6.2.2.5 Disposable Pasteur pipets and rubber bulbs.

6.2.2.6 Bottletop solvent dispenser.

6.2.2.7 40 mL vials with PFTE lined screw caps.

6.2.2.8 Volumetric flask, 100mL

6.2.2.9 Graduated cylinder, 100 ml.

6.2.2.10 Solvent waste collection jars, 125mL.

6.2.2.11 Marking pen.

6.2.3 Activated carbon cleanup

6.2.3.1 10 mL disposable pipet for use as the column.

6.2.3.1.1 All disposable carbon columns are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order).

6.2.3.2 Glass wool, precleaned with methylene chloride.

6.2.3.3 25 mL graduated cylinder

6.2.3.4 40 mL vials.

6.3 Sample Concentration Equipment.

6.3.1 Macro Concentration Equipment – Rapid-Vap

6.3.1.1 Labconco Rapid-Vap concentrator

6.3.1.2 600 mL sample concentrator tubes, Labconco or equivalent.

6.3.1.3 Borosilicate 5.75 inch and 9.0 inch disposable pipettes.

6.3.1.4 Rubber bulbs.

6.3.1.5 Borosilicate 40 mL disposable vials with PFTE lined screwcaps.

6.3.2 Macro Concentration – Snyder Column

6.3.2.1 Heating mantles with temperature controls.

6.3.2.2 Three-ball macro Snyder column.

6.3.2.3 Rubber bulbs.

6.3.2.4 Nine inch borosilicate glass pipets.

6.3.2.5 40 mL vial, with PFTE lined cap.

6.3.2.6 PFTE boiling chips.

6.3.3 Micro Concentration – N-Evap

6.3.3.1 Nitrogen blowdown apparatus (N-EVAP or equivalent).

6.3.3.2 Mini vials, 1.1 mL capacity with a tapered bottom; with PFTE faced, rubber septa and screw caps.

6.4 Sample Analysis Equipment.

6.4.1 Gas Chromatograph --- Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specification in Section 10.

6.4.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD --- 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent.

6.4.1.2 GC column for isomer specificity for 2,3,7,8-TCDF --- 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent.

6.4.2 Mass Spectrometer --- Electron impact ionization with the filament eV's optimized for best instrument sensitivity, stability and signal to noise ratio. Shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and shall meet all of the performance specifications in Section 10.

6.4.3 GC/MS Interface --- The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam

6.4.4 Data System --- Capable of collecting, recording, and storing MS data.

## 7. Reagents and Standards

7.1 Sample Pre-Treatment

7.1.1 Hydrochloric acid (HCl), concentrated 37% wt in water (ACS), Mallinkcrodt AR Select or equivalent.

7.1.2 1N HCl - Carefully add 83mL of concentrated HCl to 917 mL of reagent water in a glass container.

7.2 Aqueous Extraction

7.2.1 Acetone, pesticide quality or equivalent.

7.2.2 Toluene, pesticide quality or equivalent.

7.2.3 Methylene chloride, pesticide quality or equivalent.

7.2.4 Hexane, pesticide quality or equivalent.

7.2.5 Tetradecane, pesticide quality or equivalent.

7.2.6 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 mega ohm resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2.7 Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride, stored in a desiccator, and stored in a pre-cleaned glass bottle with fluoropolymer lined screw-cap that prevents moisture from entering.

7.3 Soxhlet extraction

7.3.1 Acetone, pesticide quality or equivalent.

7.3.2 Toluene, pesticide quality or equivalent.

7.3.3 Methylene chloride, pesticide quality or equivalent.

7.3.4 Hexane, pesticide quality or equivalent.

7.3.5 Benzene, pesticide quality or equivalent.

7.3.6 Tetradecane, pesticide quality or equivalent.

7.3.7 Sand, prepared by extracting with methylene chloride and/or baking at 450 °C for a minimum of 4 hours. After cooling store in a dessicator.

7.3.8 Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride, stored in a desiccator, and stored in a pre-cleaned glass bottle with fluoropolymer lined screw-cap that prevents moisture from entering.

7.3.9 Dry Ice.

7.3.10 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 MΩ resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.4 Waste Dilution

7.4.1 Hexane, pesticide quality or equivalent.

7.4.2 Benzene, pesticide quality or equivalent.

7.5 Acid-Base Cleanup

7.5.1 Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.5.2 Potassium hydroxide, 20% aqueous. Prepare by cautiously adding, 100 g of potassium hydroxide pellets to 400 mL of deionized water. This solution is stored at room temperature in a plastic bottle.

7.5.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in reagent grade water.

7.5.4 Hexane, pesticide quality or equivalent.

7.5.5 Benzene, pesticide quality or equivalent.

7.5.6 Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride, stored in a desiccator, and stored in a pre-cleaned glass bottle with fluoropolymer lined screw-cap that prevents moisture from entering.

7.6 Silica Gel/Alumina Column Cleanup

7.6.1 Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride, stored in a desiccator, and stored in a pre-cleaned glass bottle with fluoropolymer lined screw-cap that prevents moisture from entering.

7.6.2 Methylene chloride pesticide quality or equivalent.

7.6.3 Hexane, pesticide quality or equivalent.

7.6.4 Acetone, pesticide quality or equivalent.

7.6.5 Toluene, pesticide quality or equivalent.

7.6.6 Silica gel, Davisil Grade 923, 100-200 mesh or equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to an aluminum foil-covered Pyrex glass container then air dry and activate in an oven at 130°C for a minimum of four (4) hours. Store in labeled glass jars in desiccator until use.

7.6.7 3.3% Deactivated silica gel – To prepare add 3. 3mL of reagent water to 100 g of silica gel (section 7.6.6) in a 250 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar.

7.6.8 Acidic silica gel - To prepare, add 19 mL of concentrated sulfuric acid to 60 g silica gel (section 7.6.6) in a 250 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar.

7.6.9 Alumina, Neutral - Super I - Scientific Absorbents. Purchase and use only activated alumina. Store in an oven at 130°C when not in use.

7.6.9.1 Each new lot of alumina must be tested upon receipt and before use. Elute a solution containing all of the $^{13}C$ internal standards and native analytes through a column packed with the new lot of alumina. Collect the 5% and 60% fractions together and analyze by HRMS. Archive the 80 mL of hexane in a separate container. The target analytes and internal standard recoveries must be greater than 85% in the final fraction. If the recovery is less than 85% for any compound or internal standard, the ratios and volumes of the elution solvents must be optimized and the test repeated until all compounds meet the recovery criteria.

7.6.10 5% methylene chloride in hexane. Add 15 mL methylene chloride to 285 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.6.11 60% methylene chloride in hexane - add 390 mL methylene chloride to 210 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.7 Activated Carbon Cleanup

7.7.1 Thoroughly mix 5% (by weight) active carbon AX-21 and 95% (by weight) silica gel (Davisil Grade 923, 100-200 mesh). Activate in an oven at 130 °C for 6 hours. Store in a dessicator in an amber colored bottle with a foil lined lid until use. Do not label the bottle until oven activation is complete to avoid heat damage to the label.

7.7.2 Toluene, pesticide quality or equivalent.

7.7.3 Methylene Chloride, pesticide quality or equivalent.

7.7.4 Benzene, pesticide quality or equivalent.

7.7.5 Methanol, pesticide quality or equivalent.

7.7.6 Cyclohexane, pesticide quality or equivalent.

7.7.7 Tetradecane, pesticide quality or equivalent.

7.7.8 Hexane, pesticide quality or equivalent.

7.7.9 Acetone, pesticide quality or equivalent.

7.8 Standards and Calibration Solutions: Certified Reference Standard purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PFTE-lined caps.

7.8.1 Nonane, pesticide quality or equivalent.

7.9 Stock Solutions: Standards are used as received after being sonicated and transferred to 1.0 mL amber glass vials with PFTE lined caps.

7.9.1 Initial Calibration Standards:

7.9.1.1 1613B/8290: CS1-CS5. CIL Catalog No. EDF-9999. (See Table 5).

7.9.1.2 23/0023A/TO-9A: CS1-CS5. CIL Catalog No. EDF-4052. (See Table 6)

7.9.2 Initial Calibration Verification Standard: Wellington Laboratories Catalog No. EPA-1613-CS3.

7.9.3 Daily Calibration Verification Standards

7.9.3.1 1613B/8290: CS3. CIL Catalog No. EDF-9999-3. (See Table 7).

7.9.3.2 1613B/8290: CS3. CIL Catalog No. EDF-4141. (See Table 7).

Note: This standard may be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution.

7.9.3.3 23/0023A/TO-9A: CS3. CIL Catalog No. EDF-4052-3. (See Table 8)

7.9.4 PAR Native Standard Stock Solution: CIL Catalog No. EDF-7999 (see Table 11) 40-400 ng/mL in nonane, 200 µL.

7.9.5 Internal Standard Stock Solution

7.9.5.1 1613B/8290: CIL Catalog No. EDF-8999, (see Table 13), 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.9.5.2 23/0023A/TO-9A: CIL Catalog No. EDF-4053, (see Table 15), 1000 ng/mL ($^{13}C_{12}$-OCDD 2000 ng/mL) in nonane, 1.2 mL.

7.9.6 23/0023A/TO-9A Surrogate Standard Stock Solution: CIL Catalog No. EDF-4054, (see Table 16), 1000 ng/mL in nonane, 1.2 mL.

7.9.7 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, (see Table 14), 50 µg/mL in nonane, 1.2 mL.

7.9.8 $^{13}C_{12}$-2,3,7,8-TCDD Labeled Standard Stock Solution: CIL Catalog No. ED-900, 50 µg/mL in nonane, 1.2 mL.

7.9.9 $^{13}C_{12}$-2,3,7,8-TCDF Labeled Standard Stock Solution: CIL Catalog No. EF-904 50 µg/mL in nonane, 1.2 mL.

7.9.10 $^{13}C_{12}$-1,2,3,4-TCDD Labeled Standard Stock Solution: CIL Catalog No. ED-911, 50 µg/mL in nonane, 1.2 mL.

7.9.11 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Labeled Standard Stock Solution: CIL Catalog No. ED-996, 50 µg/mL in nonane, 1.2 mL.

7.9.12 PCDD/PCDF Window Defining and Isomer Specificity Mixture: CIL Catalog No. EDF-4147 (see Table 18 and Table 19). This standard is used for qualitative purposes only and is not considered quantitative.

7.10 Secondary Stock Solutions

7.10.1 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solution in section 7.9.7 to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.10.2 Cleanup Standard Working Stock Solution: Dilute 0.200 mL of the stock solutions in section 7.10.1 to 5.0mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.10.3 $^{13}C_{12}$ TCDD/TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions in sections 7.9.8 and 7.9.9 to 10 mL in a volumetric flask with nonane to a final concentration of 500 ng/mL.

7.10.4 Recovery Standard Secondary Stock Solution: Dilute 1.0 mL of the stock solutions in sections 7.9.10 and 7.9.11 to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.11 Standards and Spiking Solutions

7.11.1 PCDD/PCDF Window Defining and Isomer Specificity Standard: Combine 25 µL of the standard solution in section 7.9.12, 5 mL of the IS spiking solution in section 7.11.3, 5 µL of the RS stock solution in section 7.10.4, and 500 µL of nonane in a 10 mL vial. Concentrate the solution to 500 µL with a stream of nitrogen and transfer to 1.0 mL amber glass vials with PFTE lined cap.

7.11.2 PAR Native Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.9.4 to 40 mL in a graduated cylinder with acetone to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each IPAR, OPR, LCS or MS/MSD sample. See Table 11 for a complete list of compounds and their concentrations.

7.11.3 1613B/8290 Internal Standard Spiking Solution: Dilute 500 µL of the stock solution in section 7.9.5.1 to 50 mL in a graduated cylinder with acetone to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.11.4 23/0023A/TO-9A Internal Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.9.5.2 to 100 mL in a graduated cylinder with acetone to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.11.5 23/0023A/TO-9A Surrogate Standard Spiking Solution: Dilute 500 µL of the stock solution in section 7.9.6 to 25 mL in a graduated cylinder with nonane to a final concentration of 20 ng/mL. 100 µL of this solution is added to each sample train components before sampling. See Table 16 for a complete list of compounds and their concentrations.

7.11.6 Cleanup Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.10.2 to 100 mL in a volumetric graduate with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract prior to cleanup. See Table 14 for a complete list of compounds and their concentrations.

7.11.7 $^{13}C_{12}$ TCDD/TCDF Internal Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.10.3 to 100 mL in a volumetric flask with acetone to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract that are extracted for TCDD and/or TCDF analysis only.

7.11.8 Recovery Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.10.4 to 10 mL in a volumetric flask with nonane to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank, and QC sample extract.

7.12 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes should be analyzed periodically, and should be assayed against reference standards before further use.

7.13 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

## 8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log In of Commercial Samples, current revision. Sample container and preservation recommendations are listed in the table below.

**Sample Holding Times, Containers, and Preservation**

| | 1613B | 8290[1] | 23 | 0023A | TO-9A |
|---|---|---|---|---|---|
| **Holding Times** | Samples -1 year<br>Extracts – 1 year | Samples -30 days from collection<br>Extracts –45 days from extraction<br>Tissue Extracts - 45 days from collection | Samples -30 days from collection<br>Extracts –45 days from extraction | Samples -30 days from collection<br>Extracts –45 days from extraction | Samples -7 days from collection<br>Extracts –40 days from extraction |
| **Containers** | Amber Glass | Amber Glass | See KNOX-ID-0012 | See KNOX-ID-0012 | See KNOX-ID-0012 |
| **Preservation:** | | | | | |
| Aqueous Samples | 0-4 °C in the dark<br>If residual chlorine is present, add 80 mg/L sodium thiosulfate.<br>If pH > 9, adjust to pH 7-9 with sulfuric acid | 4 °C ± 2 °C in the dark | N/A | N/A | N/A |
| Solid Samples | <-10 °C in the dark | 4 °C ± 2 °C in the dark | N/A | N/A | N/A |
| Tissue Samples | <-10 °C in the dark | <-20 °C in the dark[2] | N/A | N/A | N/A |
| Air Samples | N/A | 4 °C ± 2 °C in the dark | 4 °C ± 2 °C in the dark | 4 °C ± 2 °C in the dark | ≤4 °C in the dark |

**Note:**

1 For method 8290 and 0023A the holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed may be as high as a year for certain matrices. The results of samples analyzed after the holding time expiration date should be considered to be minimum concentrations and should be identified as such in the final report. Sample extracts, however, should always be analyzed within 45 days of extraction. (For the State of South Carolina – The holdings times for 8290 are as listed in the table and are not considered recommendations.)

2 If the freezer used to store 8290 samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, a storage higher temperature is acceptable as long as it is <-10 °C.

8.2 Extracts should be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

## 9. Quality Control

9.1 Initial Demonstration of Capability

9.1.1 Initial precision and recovery (IPR) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.2 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sand or sodium sulfate spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. It is recommended that a method blank be prepared with the IPR samples.

9.1.3 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration (s) in ng/mL for each compound.

9.1.4 For each compound, compare s and X with the corresponding limits for initial precision and recovery in Table 9 for method 1613B and Table 10 for methods 8290, 23, 0023A, and TO-9A. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 The method detection limit (MDL) study described in Section 13 must be completed with acceptable results before analysis of samples may begin.

9.3 A laboratory method blank must be run along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The method blank is normally analyzed immediately after the calibration standards. The method blank consists of reagent water for aqueous samples, and a clean solid matrix (sand or sodium sulfate) for solid samples. The method blank must meet the following acceptance criteria;

- The concentration of target analytes in the method blank must be less than the MDL.
- If the concentration of target analytes in the method blank is greater than the MDL but less than the minimum level (ML), corrective action is required but the associated samples may be reported. At a minimum, corrective must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the MDL.
- If the concentration of target analytes in the method blank is greater than minimum level (ML) but less than 5% of the concentration in the associated samples, corrective action is required but the associated data may be reported. At a minimum, corrective must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the ML and documentation in the case narrative.
- If the method blank sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability

of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

- If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be done in consultation with the client.

9.3.1 The method blank internal standard recoveries must be within the established control limits. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. If the method blank internal standard recoveries are outside the QC limits and the decision is made to report the sample results, an NCM must be initiated and the reason for accepting the sample results clearly documented. Consultation with the client before acceptance must take place.

9.3.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," an NCM is initiated and appropriate comments made in the report narrative to provide further documentation.

9.3.3 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical run. This is accomplished by analysis of a method blank if available. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample (LCS) or Ongoing Precision and Recovery (OPR)

9.5.1 An LCS/OPR sample is analyzed along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. LCS/OPR spike components, concentrations, and control limits are given in Table 11.

9.5.2 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the LCS/OPR sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

- If the batch is not re-extracted and reanalyzed, an NCM must be initiated and the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of an acceptable reason for not reanalyzing might be that the matrix spike and matrix spike duplicate recoveries are within control limits, the method blank and sample internal standard recoveries are within limits, and the data clearly demonstrates that the problem was confined to the LCS/OPR).
- For method TO-9A calculate the precision (%D) relative to the previous TO-9A LCS. The precision must be within ± 30%.

9.5.3 Ongoing monitoring of the LCS/OPR provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Internal Standards.

Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 for methods 1613B and 8290 or in Table 15 for methods 23, 0023A, and TO-9A.

9.6.1 If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than the lower control limit, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the minimum levels (ML's), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (ML's), re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 12). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is

within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented in the report narrative.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the analysis is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCSD should be analyzed. The LCSD is evaluated using the same acceptance criteria as the LCS. The RPD of the LCS and LCSD are compared to the acceptance limits in Table 12.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.8 Surrogate Standards – Methods 23, 0023A, TO-9A

Field surrogate standards are added to the collection media prior to sample collection when performing methods 23, 0023A, or TO-9A. The surrogate recoveries are calculated relative to the internal standards and are a measure of sampling efficiency. The recovery of the surrogate standards should be within the limits specified in Table 16. Poor recoveries of the surrogate standards may indicate breakthrough in the sampling train.

9.8.1 If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Flag the results that are outside control limits and notify the Project Manager. The client must be notified and consulted for additional corrective action.

## 10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 5 for methods 1613B and 8290 or in Table 6 for methods 23, 0023A, or TO-9A. Store calibration standards at room temperature in the dark. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). For method 1613B adjust the GC conditions to meet the relative retention times for the PCDDs/PCDFs listed in Table 3. The cycle time for MID descriptors must be ≤ 1 sec.

10.2.3 By using a PFK molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to the m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 is greater than 10,000 (10 percent valley).

10.2.4 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.5 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution or Mixture Solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDF}} \times 100$$

10.2.6 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 3 for methods 1613B and 8290 or in Table 4 for methods 23, 0023A, and TO-9A using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7 Calculate the mean relative response factor and the standard deviation of the relative response factors using the equations in the LQM for each calibration standard solution.

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met for each initial calibration standard before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, follow the procedure in STL Policy P-T-001(see reference section 16.9).

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors must be within the acceptance criteria listed in Table 5 for methods 1613B and 8290 or in Table 6 for methods 23, 0023A, and TO-9A.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 22.

10.2.8.4 For method 1613B the absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.9.2. Calculate the concentration of the ICV using the RRF's from the CS3 standard analyzed in section 10.2.6. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:
$C_{Exp}$ = The expected concentration of the ICV Standard.
$C_{Calc}$ = The calculated concentration of the ICV Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is less than or equal to ±35% for all native and labeled compounds. The warning limits for percent difference is ±35 - 55%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits shall be documented as an NCM. Corrective action must be taken and may include the following

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A calibration check is also required at the end of a 12 hour period when performing method 8290 or 0023A.

10.3.2 Document the mass resolution performance as specified in section 10.2.3. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.4 and 10.2.5.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations using the formulas in section 12.3.

> Note: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.9.3.2 may be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period that samples are analyzed. If acceptable beginning continuing calibration criteria is not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive beginning continuing calibration does not meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing beginning continuing calibrations by the analysis of two consecutive acceptable beginning continuing calibrations or by analysis of a new initial calibration.

10.3.5.1 The measured concentration or percent difference for each compound must be within the acceptance criteria limits in Table 7 for methods 1613B and 8290 or in Table 8 for methods 23, 0023A, and TO-9A.

10.3.5.2 For method 1613B the relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 3.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) ≥ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 22.

10.3.5.5 When performing method 8290 or 0023A, if the continuing calibration fails at the beginning of a 12-hour shift, the instructions in section 10.3.5 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than ±25 percent RPD for unlabeled native analytes and ±35 percent RPD for labeled standards, the closing standard may not be used as a beginning calibration standard for the next 12-hour shift and the requirements in section 10.3.5 must be met before analysis may continue. Use the mean RRF from the two daily continuing calibration runs to compute the analyte concentrations, instead of the RRFs obtained from the initial calibration. If the continuing calibration check performed at the end of a 12 hour period fails by more than ±25 percent RPD for unlabeled native analytes and ±35 percent RPD for labeled standards initiate corrective action and reanalyze all positive sample extracts analyzed during the 12 hour period encompassing the failed end of shift calibration check.

> It is realized that it may not always be possible to achieve all RF criteria. For example, the RF criteria for 13C12-HpcDD and 13C12-OCDD were not met, however the RF values for

the corresponding unlabeled compounds were within the criteria established in this procedure. The data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must consult with the group manager and the project manager to assess the impact on the data quality objectives on the affected samples. Corrective action must be taken and any decision to report sample data in this situation must be made in conjunction with the client. An NCM must be initiated if the data is to be reported.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard.

10.3.6.1 For methods 1613B, 23, TO-9A The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

10.3.6.2 For method 8290, 0023A - The Continuing Calibration Standard check and mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12-hour shifts, the Window Defining Mixture and/or Column Performance Solution Mixture must be analyzed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

## 11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Sample Pretreatment

11.2.1 Tissue Samples

11.2.1.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is blended to provide a homogeneous sample. At least 20 g of tissue should be homogenized if possible to allow for reanalysis if necessary.

11.2.1.2 Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender.

11.2.1.3 Weigh out 10 grams of the homogenized tissue sample. Add the 10 g sample along with 20 g of sodium sulfate to a laboratory blender. Blend the tissue/sodium sulfate mixture, while adding dry ice as necessary, to achieve a powder like consistency.

11.2.1.4 Record the sample and weight on the sample prep sheet or in a logbook.

11.2.2 Fly Ash Samples

11.2.2.1 If the sample matrix is fly ash and is to be analyzed by method 8290, pretreat the sample with HCl as follows:

11.2.2.2 Weigh 10±0.05 g of the fly ash sample and transfer to a 240 mL glass jar. Record the sample and weight on the sample prep sheet. If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD samples.

11.2.2.3 Add 1.0 mL of the internal standard spiking solution (see section 7.11.3) to the sample. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry. Add 150 mL of 1N HCl to the sample. Seal the jar with a PFTE lined screw cap and shake for 3 hours at room temperature.

11.2.2.4 Rinse a glass fiber filter with reagent water, and filter the sample through the filter paper, placed in a Buchner funnel, into a 1 L flask. Rinse the sample bottle twice with small amounts of reagent water, making sure that all particulate matter is transferred onto the glass fiber filter. Wash the fly ash cake with approximately 500 mL organic-free reagent water.

11.2.2.5 Extract the sample and glass fiber filter by Dean-Stark Soxhlet extraction in section 11.4.

11.3 Aqueous Sample Extraction

11.3.1 Remove the samples from the refrigerator several hours before extraction and allow them to come to room temperature before measuring the volume or performing the extraction. Inspect the sample for solids or biphasic sample characteristics. If either condition exists, document the observation on the sample tracking sheet and consult the project manager for further instructions (see 11.3.6.1 – 11.3.6.4.4 below). If visible solids are present determine the percent solids using the following procedure

11.3.1.1 Add 10 mL of the well shaken sample to a pre-weighed aluminum weighing dish. Weigh the dish to three significant figures. Dry the dish overnight in an oven at 105 °C. Reweigh the dish and calculate the percent solids using the following equation.

$$\%solids = \frac{\text{weight of dish plus sample after drying} - \text{weight of dish}}{\text{weight of dish plus sample before drying} - \text{weight of dish}} \times 100$$

11.3.1.2 If the sample contains >1 percent suspended solids, a sample aliquot sufficient to provide 10 grams of dry solids is used and the sample is extracted following the procedure in section 11.4. If excess liquid is present, the sample may be filtered and the solids and filter extracted as in section 11.3.6.4.

11.3.1.3 If the sample contains ≤1 percent suspended solids the sample is filtered through a Buchner funnel with a 2.7 um glass fiber filter following the procedure in section 11.3.6.4.

11.3.2 Refer to Knoxville SOP, KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire and replace any glassware found to be damaged.

11.3.3 Place separatory funnels, one for each sample, the method blank, and the OPR, in the positions in the rotary extractor.

11.3.4 Place a 600 mL concentration tube directly beneath each separatory funnel in the tube holder.

11.3.5 Plug a glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the funnel stops dripping, place the funnel on top of the concentrator tube.

11.3.6 If solids are not observed in the sample, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. Using a 1000 mL graduated cylinder measure out 1000 mL of reagent water and add to the separatory funnels marked for the method blank , LCS/OPR, and LCSD (if required).

11.3.6.1 If the sample exhibits biphasic characteristics, the sample can either be mixed and extracted as an aqueous sample or the phases can be separated and extracted individually. The decision as to which approach to use should be made in consultation with the Project Manager and the Client. Document the decision process as well as the characteristics and relative volumes of each sample phase.

11.3.6.2 For method 8290, if the sample appears to have a solids content of >1% or is biphasic, the project manager is contacted to determine if the client wants the sample filtered. If so, follow the procedure in section 11.3.6.3. The particulates on the filter and the filter itself may be extracted by Soxhlet extraction following the procedure section 11.4. The resulting extract is combined with the extract of the aqueous portion during the concentration step.

11.3.6.3 For method 1613B, if the visible solids appear to be ≤1 percent (≤10g/L of sample) follow the procedure in section 11.3.6.4. If the visible solids appear to be >1 percent follow the procedure in section 11.3.6.4.5.

11.3.6.4 Sample Filtration

11.3.6.4.1 Assemble a Buchner funnel with a rubber stopper on top of a clean filter flask. Insert a 2.7 um glass fiber filter into the funnel. Wet the filter paper with a few mLs of reagent water and apply vacuum to the filter flask.

11.3.6.4.2 Apply vacuum to the flask, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.3.6.4.3 Rinse the sample bottle twice with approximately 10 mL portions of reagent water to transfer any remaining particles onto the filter. Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.3.6.4.4 If the percent solids are ≤1 percent, extract the filtrate in a separatory funnel by proceeding to section 11.3.7. Extract the solids on the filter and the filter itself following the procedure

in section 11.4. **Do not add internal standards to this portion of the sample, only add internal standards to the aqueous portion of the sample!** The resulting extract is combined with the extract of the aqueous portion during the macro concentration step in section 11.6.

11.3.6.4.5 If the percent solids is not ≤1 percent, extract the particulates on the filter and the filter itself following the procedure in section 11.4 otherwise follow the instructions in section 11.3.6.4.4.

11.3.7 Using a Class A 1 mL volumetric pipet, add 1 mL of the $^{13}C$ labeled internal standard spiking solution, as specified in section 7.11.3, to each sample, the method blank, LCS/OPR, LCSD, and MS/MSD (8290 only) samples . Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

11.3.8 Using a Class A 1 mL volumetric pipet, add 1 mL of the PAR native spiking solution, as specified in section 7.11.2, to the designated LCS/OPR, LCSD (if required), and MS/MSD (8290 only) samples. Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

Note: If the volume of standard in the stock container is less than 10mL after use, discard the remaining portion and prepare a new batch as specified in section 7.11.2.

11.3.9 Add 60 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel. Add 60 mL of methylene chloride to the method blank, LCS/OPR , and LCSD (if required) as well.

11.3.10 Securing the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles may be worn when performing this procedure.

11.3.11 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.3.12 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the concentrator tube. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed. If at least 10 minutes has elapsed and other ways of breaking up or reducing the size of the emulsion have failed the following steps may be tried to reduce the impact of the emulsion on the sodium sulfate.

11.3.12.1 Place a large piece of pre-cleaned glass wool in the funnel containing the sodium sulfate.

11.3.12.2 Spread the glass wool out, covering the entire surface of the sodium sulfate to about a depth of about 5 to 10mm. If the emulsion is hard to break up and persistent, a small, additional layer of sodium sulfate may be added on top of the glass wool.

11.3.12.3 Drain the solvent and emulsion layer into the funnel being careful to drain no more than 60 mL of volume if a clear phase layer cannot be determined.

11.3.12.4 If this procedure is used the funnel should be rinsed with an extra 30ml of methylene chloride to ensure all analytes are rinsed into the concentrator tube after the third portion of methylene chloride has drained through the sodium sulfate in section 11.3.14.

11.3.13 Repeat steps 11.3.9 through 11.3.12 two more times.

11.3.14 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.3.15 Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.3.16 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the volume of sample used on the benchsheet.

11.3.17 Proceed to Macro Extract Concentration by Rapid-Vap in section 11.7.

11.4 Soxhlet Extraction

11.4.1 Prepare and label the required number of Soxhlet systems.

NOTE: If samples have a high water content (e.g., sludges, pulp samples, etc.) or are to be extracted by method 1613B, a Dean-Stark extractor should be used to remove the water from the sample. The Dean-Stark apparatus is installed between the Soxhlet body and the condenser when the components are assembled.

11.4.1.1 The Soxhlet is prepared by cleaning and rinsing per section 6.1.

11.4.2 Transfer 10±0.05 g of the solid sample (wet weight) into a glass fiber extraction thimble or glass fiber filter paper and put the thimble or filter inside the Soxhlet. If tissue samples are being extracted, add the entire sample and sodium sulfate mixture prepared in section 11.2.1.3. Record the sample and weight on the sample prep sheet. Initial and date the entry. If a sample is designated for MS/MSD analysis (8290 only), prepare two additional portions of the sample and label them as the MS and MSD samples.

Note: The MS and MSD samples must be prepared at the same weight as the OS to avoid calculation errors in the RPD values.

11.4.2.1 For the method blank, LCS/OPR and LCSD (if required) add 10±0.05 g of sand or sodium sulfate to a glass fiber extraction thimble.

11.4.2.2 If the matrix is tissue samples, sodium sulfate and dry ice are used for method blank, LCS/OPR, and LCSD (if required). Transfer 20±0.5 g of the sodium sulfate and several small chips of dry ice into an extraction thimble.

11.4.2.3 Record the blank matrix type and lot number on the bench sheet.

11.4.3 Pour approximately 350 mL toluene into a 500 mL round bottom flask. Place the flask in the heating mantle. Add 10-15 boiling beads and several PFTE boiling chips.

11.4.4 Place the extraction thimble in the glass Soxhlet extractor.

11.4.5 Assemble the Soxhlet system and secure to the lab supports.

11.4.5.1 Place the method blank and QC samples in random positions within the available prep positions in the hood (i.e., do not use the same positions each time the method blank and QC samples are prepared). Record the condenser position and Soxhlet set number for the method blank.

11.4.6 Spike each sample with 1.0 ml of the internal standard spiking solution (see section 7.11.3) and add a small amount of glass wool if needed to the top of the extraction thimble. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

Note: Omit this step if internal standards have been previously added to fly ash samples during acid pre-treatment (section 11.2.2.3).

11.4.6.1 Spike the LCS/OPR, LCSD (if required), and MS/MSD (8290 only) samples with 1.0 ml of the PAR native spiking solutions (see section 7.11.2) prior to adding the glass wool. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

Note: If the volume of standard in the stock container is less than 10mL after use, discard the remaining portion and prepare a new batch as specified in section 7.11.2.

11.4.7 Adjust the temperature of the heating mantle to bring the toluene in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour. Record the date and time that the Soxhlet extraction was started on the benchsheet and initial and date.

11.4.8 Soxhlet extract the sample in the above manner for a minimum of 16 hours. At the end of the extraction period turn off the heating mantles. Record the date and time that the Soxhlet extraction was completed on the benchsheet and initial and date.

11.4.9 Remove the condensers and empty the Soxhlet extractor chamber, then remove the Soxhlet extractor from the 500 mL round bottom flask.

11.4.10 Add several (2-3) fresh boiling chips to the flasks. Insert a three-ball macro Snyder column into the top of the 500 mL round flask.

11.4.11 Place the 500 mL flask back into the heating mantle and reduce the extract volume to approximately 10-15 mL.

11.4.12 Transfer the extract into a 40 mL vial containing 100 uL of tetradecane, rinsing the 500 mL flask 3 times with 3 mL of toluene. Add the rinsings to the 40 mL vial.

11.4.13 Place the 40 mL vials into the nitrogen concentration device and reduce the volume to near dryness. Add 4 mL of hexane and swirl the vial. Reduce the volume of hexane to near dryness again to complete the solvent exchange. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the residue. Adjust the final volume of the extract with hexane to 12 mL for acid-base cleanup or 2 mL for column cleanup. Proceed to sample cleanup in section 11.8.

11.5 Waste Dilution

11.5.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.5.2 Tare a clean 40 mL VOA vial on a laboratory balance. Add an appropriate amount of sample (e.g., 1.0 g) to the VOA vial. If a sample is designated for MS/MSD analysis (8290 only), prepare two additional portions of the sample and label them as the MS and MSD samples. Prepare method blank, LCS/OPR, and LCSD (if required) samples by adding 12 mL of hexane to a 40 mL VOA vial.

11.5.3 Record the weights and volumes used on the laboratory bench sheets and initial and date.

11.5.4 Add 1.0 ml of the internal standard spiking solution (see section 7.11.3) to the samples, method blanks, and QC samples. Record the spike solution number and the volume spiked on the sample prep sheet. Initial and date the entry. Add hexane to bring the volume to 12 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the sample.

11.5.5 Add 1.0 ml of the PAR native spiking solutions (see section 7.11.2) to the LCS/OPR, LCSD (if required), and MS/MSD (8290 only) samples. Record the spike solution identification number and the volume spiked on the sample prep sheet. Initial and date the entry.

11.5.6 Proceed to sample extract cleanup in section 11.8.

11.6 Air Sampling Trains

11.6.1 For media and sample preparation of air sampling trains refer to Knoxville SOP, KNOX-ID-0012.

11.7 Macro Extract Concentration by Rapid-Vap

11.7.1 Preheat the unit to the appropriate temperature for the solvent used in the extraction.

11.7.2 Set the operating parameters on the programmer. For example, if there is 300 ml of a methylene chloride extract, the following parameters may be used and should be adjusted as needed:

| | |
|---|---|
| Temperature | 30 °C |
| Vortex Speed | 30%, to be increased at a later time |
| Nitrogen | 7-9 psi |
| Timer Set | 30 minutes |

11.7.3 Place 600 ml concentrator tubes containing the extract in the Rapid-Vap. Begin concentrating the extract, adjust the vortex speed for the proper rate of concentration.

11.7.4 When the extract has been concentrated to less than 20 mL, add approximately 60 mL of hexane. Concentrate the extract to a final volume of approximately 2 ml. Shut off the nitrogen flow and turn off the Rapid-Vap or remove the 600 mL concentrator tube to prevent further concentration.

11.7.5 Transfer the extract to a 40 ml vial with a 9" disposable pipet, rinsing the sample tube three times with 3 ml of hexane. Reduce the volume in the 40 mL vial using the N-Evap to approximately 2 ml and proceed to extract cleanup in section 11.8. If no additional cleanups are to be performed continue with the following steps to dry the extract.

11.7.6 Prepare a small funnel by putting a small plug of pre-cleaned glass wool to the bottom of the funnel and adding a layer of sodium sulfate on top of the glass wool.

11.7.7 Pipet the extract from the Rapi-Vap concentrator tube and through the funnel containing the sodium sulfate into a 40ml vial.

11.7.8 Rinse the concentrator tube 3 times with approximately 3ml of hexane for each rinse. The sodium sulfate funnel then should be rinsed with an additional 2ml of hexane. Proceed to micro concentration in section 11.9.

11.8 Sample Extract Cleanup

11.8.1 For 1613B samples, add 1.0 mL of the $^{37}$Cl-,2,3,7,8-TCDD cleanup standard (see section 7.11.6) to each sample extract as well as the method blank and OPR sample extracts.

11.8.2 Acid-Base Cleanup

The acid-base cleanup is employed when sample extracts are colored and/or oily in appearance, or if specified by the client or project manager.

11.8.2.1 Bring the extract volume up to ~15 mL with hexane in a 40 ml vial.

NOTE: If the extracts are from fish tissue, omit sections 11.8.2.2 and 11.8.2.3.

11.8.2.2 Wash the extract by adding 10 mL of 20% aqueous potassium hydroxide to the vial and gently shaking for 20 seconds. If an emulsion begins to form, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the base washing until no color is visible in the base layer (perform a maximum of four base washings).

11.8.2.3 Add 10 mL of 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion.

11.8.2.4 Slowly add 15 mL of concentrated sulfuric acid to the vial and shake for 30 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.8.2.5 Add 10 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.8.2.6 Reduce the extract volume to approximately 2 ml.

11.8.2.7 Proceed to section 11.8.3, silica gel/alumina column cleanup.

11.8.3 Silica gel/alumina column cleanup

Silica gel/alumina column cleanup is employed when sample extracts are clear or after other cleanup techniques have been employed. If treated drinking water samples are being analyzed, further cleanup may not be necessary.

11.8.3.1 Prepare a 20mm diameter column and a 16mm diameter column for each extract by rinsing, in order, with acetone, toluene, methylene chloride and hexane. Place a large ball of pre-cleaned glass wool in the bottom of each column.

11.8.3.2 Mark the level to which the column packings will be added with a marking pen starting at the top of the glass wool plug and proceeding from bottom to top. The levels for each type column are as follows;

20 mm Silica Gel column
12 mm – 2g of 3.3% deactivated silica gel
16 mm – 4g of acidic silica gel
12 mm - 2g of 3.3% deactivated silica gel
10 mm – sodium sulfate

16 mm Alumina Column
40 mm – 6 g of neutral alumina
10 mm – sodium sulfate

11.8.3.3 Place the columns to the lab supports in the hood so that the 20 mm silica gel column is above the 16 mm alumina column. Offset the columns slightly so that the packings can be added and the columns rinsed.

11.8.3.4 Add the column packing in the order listed above while tapping with a marking pen to column to settle the contents to prevent channeling. When the columns have been completely packed, remove the lower columns from the support rack and remove the ink markings with a paper towel moistened with methylene chloride. Replace the columns in the rack.

11.8.3.5 Place a 125ml glass jar under the lower alumina column to catch the solvent wastes and eluants as they filter through the column.

11.8.3.6 Measure out 60ml of Hexane using a graduated cylinder and pour it into a 100ml volumetric flask, one flask for each set of columns, to be used later in the procedure. Do not use this hexane for the column rinsing in the next section.

11.8.3.7 Add 20 ml of hexane to each column to rinse the packing. Collect the hexane from the columns in the 125 mL glass jar, the columns must be aligned so that the waste does not drip on the surface of the hood. When the level of solvent in the silica gel column approaches the top of the packing, move the upper column support so that the tips of the upper columns are inserted into the tops of the lower columns and the solvent will drip into the lower columns.

11.8.3.8 Just as the level of hexane reaches the top of the packing in the silica gel column transfer the sample extract into the top of the column. Rinse the extract vial 3 times with 1.5ml of Hexane and add each of these rinsings to the silica gel column.

11.8.3.9 Just as the solvent level reaches the top of the column packing pour the 60ml of hexane into the top of the silica gel column and allow this to drip into and through the alumina column and into the collection jar. When the hexane has completely drained from the silica gel column, remove the column from the support rack and dispose of it in the appropriate waste container.

11.8.3.10 Just as the level of hexane reaches the top of the packing in the alumina column using a solvent dispenser add 10ml of 5% methylene chloride/hexane mixture. Immediately after adding the 5% mixture replace the 125 mL glass jar containing the solvent waste with 40ml vial which has been labeled with the sample workorder number. Dispose of the solvent waste in the 125 mL glass jar in the appropriate waste collection container.

11.8.3.11 Just as the level of the 5% mixture reaches the top of the packing in the alumina column add 30ml of 65% methylene chloride/hexane using a solvent dispenser and continue to catch the eluants in the 40ml vial.

11.8.3.12 When the solvent has completely drained from the alumina column, cap the 40 mL vial containing the eluant and dispose of the alumina column in the appropriate waste container.

11.8.3.13 If no further cleanup is to be performed, proceed to final extract micro concentration. Otherwise, reduce the volume of the extract to approximately 2ml using the nitrogen micro concentration apparatus and proceed to the next cleanup.

11.8.4 Activated carbon cleanup

Carbon column cleanups should be performed when site history indicates carbon columns are necessary for removal of interferences. Carbon columns should also be run if, when running the extracts through dual columns, it is noticed that the acid silica layer becomes colored along the entire length of the acid silica.

11.8.4.1 Prepare a 10 mL disposable pipette by cutting off the tapered end to achieve a 12-cm column. Insert a glass-wool plug of about 1 cm in length at one end and pack the column with 4.1 cm of the of the AX-21 Carbon/Silica Gel mixture. Hold the packing by inserting an additional glass wool plug, again about 1 cm in length, in the other end.

11.8.4.2 Pre-elute the column with 10 mL of cyclohexane/methylene chloride (50:50 v/v). Turn the column over and pre-elute in the opposite direction with another 5 mL of cyclohexane/methylene chloride (50:50 v:v).

11.8.4.3 When the solvent reaches the glass wool, add the sample extract. Rinse the sample vial 2 times with 2 ml of 50/50 cyclohexane/methylene chloride. Add these rinses to the column. Elute the column with the following sequence of solvents:

11.8.4.3.1 6 mL of cyclohexane/methylene chloride (50:50 v/v).

11.8.4.3.2 5 mL of methylene chloride/methanol/benzene (75:20:5 v/v).

11.8.4.4 Allow the 75:20:5 methylene chloride/methanol/benzene to drain completely. Turn the column over and in the direction of reverse flow elute the PCDD/ PCDF fraction with 25 mL toluene into a 40 mL vial containing 100 uL of tetradecane.

11.8.4.5 Place vials containing the extract in the nitrogen concentration apparatus and reduce the solvent volume to approximately 0.3 ml.

11.9 Micro Extract Concentration by Nitrogen Blowdown.

11.9.1 When all cleanups have been completed on the sample, add 20 uL of the labeled recovery standard spiking solution (see section 7.11.8) to an empty clean 1.1 ml tapered minivial that has been labeled with the sample ID. Mark the level of the recovery standard on the minivial (mark half the level, 10 µL, if the extracts are from treated drinking waters). Record the volume of recovery standard added on the benchsheet.

11.9.2 Transfer the concentrated extract into the mini-vial. Rinse the 40 ml vial at least twice with a small amount of hexane and add the rinses to the minivial. Put the minivial on the N-EVAP nitrogen blowdown and reduce the volume to the mark on the vial. Put the cap with PFTE-faced septa securely on the vial. Record the final extract volume on the benchsheet.

11.9.3 All items listed on the data review check list must be checked by both the prep analyst who performed the extraction and cleanups and the prep analyst who performed the second level review. An example data review check list is shown in Figure 4.

11.9.4 Transfer the extracts and paperwork to the GC/MS group for analysis.

11.10 Sample Extract Analysis

11.10.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data until OCDF has eluted from the column.

11.10.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename
Analyst
Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.10.3 Generate ion chromatograms for the masses listed in Table 21 that encompass the expected retention windows of the PCDD and PCDF homologous series.

## 12. Data Analysis and Calculations

12.1 Refer to Figure 4 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.2.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.2.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.2.3 The ratio of the integrated areas of the two exact m/z's specified in Table 21 must be within the limits specified in Table 22, or alternatively when performing method 1613B, within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.2.4 Method 1613B only - The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 3.

12.2.5 Method 8290 and 0023A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within -1 to +3 seconds of the isotopically labeled standard.

12.2.6 Method 23 and TO-9A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within ±3 seconds of the isotopically labeled standard.

12.2.7 Method 8290, 23, 0023A, and TO-9A only - For 2,3,7,8-substituted isomers, which do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration.

12.2.8 The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.4.

12.2.9 No peaks detected in the polychlorinated diphenyl-ether (PCDPE) mass channel in the same retention time region (± 2 sec for method 8290 & 0023A) as a PCDF peak.

12.3 Quantitation for PCDD's and PCDF's.

12.3.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$Ris = \frac{Ais \times Qrs}{Ars \times RRFis \times Qis} \times 100\%$$

where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

Note: In some situations, such as high-volume water sampling or air train samples, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = \frac{Crs \times Vrs}{S}$$

Where:
Qrs = ng of recovery standard added to extract
Crs = concentration of recovery standard added to the split portion of the extract
Vrs = volume of recovery standard added to the split portion of the extract
S = split ratio of the extract (decimal fraction of the extract used)

12.3.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards. The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:
Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.
Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.
Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.3.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard should be within the limits specified in Table 13 for method 1613B or 8290 or in Table 15 for method 23, 0023A, or TO-9A. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the internal standard. If the S/N is $\geq$ 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed.

12.3.4 Calculate the concentration of target analytes according to the following equation:

$$C = \frac{Ata \times Qis}{Ais \times RRF \times Ws \times Ssl}$$

Where:

Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a particular level of chlorination, the average of the individual 2,3,7,8-isomer RRF's is used in the calculation.

12.3.6 Calculate the total concentration of all isomers within each homologous series of PCDD's and PCDF's by summing the concentrations of the individual PCDD or PCDF isomers.

12.3.7 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRFs \times Ws \times Ssl}$$

Where:

N = average peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRFs = mean relative response factor of compound for the shift opening and closing standards
W = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.8 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.2.3, calculate an Estimated Maximum Possible Concentration (EMPC). Two different calculation formulas may be used depending upon specific client requirements.

12.3.8.1 When performing method 8290 for EPA regulated analyses where the currently promulgated method is required by law (e.g. Trial Burns) and for all other analyses unless the client has

specified otherwise, use the equation in section 12.3.4, except that Ata should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.3.8.2 When the client has specifically requested, use the equation in section 12.3.4 without correcting the areas. This method will give an EMPC which is always higher than the method above and would be considered the worst case.

12.3.9 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of the peak using the equation in section 12.3.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.3.10 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For the other congeners (including OCDD and OCDF), however, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Dilutions of up to 1/10 may be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed.

12.3.11 Evaluate the ion chromatograms of the PFK lock mass and calibration mass for each MID group. The PFK mass intensity should be consistent throughout the retention time of the target compounds. Negative excursions or variations in the PFK mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results should be carefully evaluated when there is evidence of ion suppression present in the PFK mass traces.

12.4 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.5 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\,\text{min} \times Vfe}{Ws}$$

Where:

Cmin = the concentration the analyte in the lowest calibration standard
Ws = amount of sample spiked and extracted (grams or liters)
Vfe = the final volume of the extract, corrected for all splits and dilutions

$$Vfe = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.6 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$MaxL = \frac{C\,\max \times Vfe}{Ws}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard
Vfe and Ws are defined in Section 12.5.

12.7 Flag all compound results in the sample that were detected in the method blank with a "B" qualifier.

12.8 Flag all compound results in the sample that are below the minimum level with a "J" qualifier.

12.9 Flag all compound results in the sample that are above the upper calibration limit with an "E" qualifier.

12.10 Flag all compound results in the sample that are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.11 Flag compound results in the sample that exhibit chromatographic evidence of co-eluting compounds with a "C" qualifier.

12.12 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier.

12.13 Data review

12.13.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.13.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.13.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.13.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.13.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. An example data review check list is shown in Figure 4.

## 13. Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP S-Q-003, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in STL Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

## 14. Pollution Prevention

14.1 All procedures shall be conducted in a manner to minimize, as far as practical, the use of solvents, reagents and other chemicals.

## 15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Waste methylene chloride from quartz fiber filter preparation, PUF adsorbent preparation, XAD-2 resin preparation, PUF/XAD-2 cartridge preparation, glassware rinsing and sodium sulfate pre-rinsing shall be placed in the flammable waste stream, contained in a steel satellite accumulation container type or flammable solvent container.
- Waste acetone and hexane from glassware and acid rinsing shall be placed in the flammable waste stream, contained in a steel satellite accumulation container type or flammable solvent container.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous shall be placed in the incinerable laboratory waste stream, contained in a poly satellite accumulation container.
- Extracted PUF filters, XAD-2 resin, paper funnel filters, glass wool, fish/crawfish and soil contaminated with methylene chloride shall be placed in the incinerable laboratory waste stream, contained in a poly satellite accumulation container.
- Contaminated sulfuric acid used during extract cleanup shall be placed in the acidic laboratory waste stream, contained in a poly satellite accumulation container or 55 gallon poly drum.
- Extracted aqueous samples, contaminated with methylene chloride shall be placed in the organic water waste stream, contained in a poly satellite accumulation container.
- Silica gel, alumina, carbon and sodium sulfate, from column clean-ups, contaminated with various solvents and eluates shall be placed in the incinerable laboratory waste stream, contained in a poly satellite accumulation container.

## 16. References

16.1 STL Quality Management Plan (QMP), current revision.

16.2 STL Knoxville Laboratory Quality Manual (LQM), current revision.

16.3 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins And Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994

16.4 USEPA SW-846 "Test Methods for Evaluating Solid Waste" Third Edition, Method 8290 and 0023A.

16.5 USEPA Method 23 – Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. 40 CFR Part 60 Appendix A.

16.6 Method TO-9A: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition EPA/625/R-96/010b.

16.7 STL SOP, KNOX-ID-0012, Method 0023A and Method 0010 Sampling Train Pre-Sampling Preparation and Sample Extraction Procedure (Includes TO-9A Sampling Components).

16.8 STL SOP, KNOX-QA-0002, Glassware Cleaning, current revision.

16.9 STL Policy, P-T-001, Selection of Calibration Points.

## 17. Miscellaneous

17.1 Deviations from reference method.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 Method 1613B employs a gravimetric determination of sample size rather than a volumetric determination. This procedure employs a volumetric determination of sample size to allow reporting of sample concentration in the standard units of pg/L (ppq). This modification has no impact on the performance criteria of this method.

17.1.3 The solids determination has been modified from that specified by method 1613B. The modification reduces the sample prep turnaround time by eliminating the need to perform solids determinations on every aqueous sample with visible particles. This modification has no impact on the performance criteria of this method.

17.1.4 The determination of solids content procedure used for aqueous samples is the same as the 1613B procedure used for solid samples rather than the 1613B procedure for aqueous samples. The aqueous sample procedure in 1613B is subject to error if the sample density is not exactly 1.0 g/mL.

17.1.5 The amount of hexane used in the solvent exchange step has been reduced from that specified in the reference methods. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.6 Method 1613B specifies that the sample bottle is rinsed twice with 5 mL of reagent water after the sample is transferred to the separatory funnel. This procedure specifies that the sample bottle is rinsed three times with methylene chloride after the sample is transferred to the separatory funnel. This modification improves the removal of target compounds from the sample bottle.

17.1.7 The separatory funnel is only rinsed once with methylene chloride after the sample is extracted instead of three times as specified in Method 1613B. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.8 Toluene volumes and cycle rates for Soxhlet extractors have been optimized for the specific size of glassware used and may not be the same as those specified in the referenced method. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.9 Soxhlet extracts are not filtered before concentration and solvent exchange. The use of glass wool in the extraction thimbles eliminates the transfer of particles to the extraction solvent. The column cleanup procedures remove any particulate that may not be removed by the glass wool. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.10 Extraction amounts are based on wet weight as opposed to the adjusted amount based on percent moisture as specified in method 1613B. Particle size determination and reduction as specified in method 1613B is not performed on a routine basis. Silica and sand is not added to the Soxhlet extraction thimble as specified in method 1613B. Fish tissues are extracted with toluene rather than methylene

chloride/hexane as specified in method 1613B. These procedures are considered to be outside the scope of the laboratories routine extraction procedures and are only performed on a client specific or project specific basis. These procedures, if required, will be specified and documented in the appropriate QAPPs.

17.1.11 Benzene is used to aid in dissolving the samples and/or extracts in hexane. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.12 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.13 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.14 The acid-base cleanup procedure is carried out in a VOA vial instead of a separatory funnel. Disposable glassware is used to decrease the risk of cross contamination. The volumes of the washes used have been adjusted for use in the VOA vials. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.15 The silica gel/alumina column cleanup used in this procedure has been optimized relative to amount and order of packings and may vary from the various columns and packings specified in the referenced methods. The solvent volumes and mixtures have been optimized based on evaluation of the elution of native and labeled standards. The silica gel and alumina are heated in an oven at 130 °C instead of 110 °C. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.16 The carbon column used in this procedure is based on the column specified in method 8280. Silica gel is used as the carbon column support instead of Celite 545® as specified in methods 8290 and 1613B. It has been determined that silica gel is less likely to contain contaminants and interferences which are not removed by the a precleaning procedures than Celite 545®, yet performs similarly. The solvents and elution schemes used re as specified in method 8280 rather than 8290 and 1613B. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.17 Method 8290 does not require dilution and reanalysis of samples for which OCDD exceeds the calibration range. Although this allowance is not made by method 1613B, this procedure does not require dilution for OCDD on samples analyzed by that method.

17.1.18 The calibration standards specified in method 23 are used for method 0023A and TO-9A.

17.1.19 Extracts are stored at room temperature rather than at <10 °C. The reference method requires that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with

precipitation. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.2 Summary of modifications to SOP

17.3 Summary of revisions to SOP for revision 6.

17.3.1 Added an exception to 1613B allowing OCDD over calibration range.

17.3.2 Added RLs for biological tissues in Table 2.

17.3.3 Added health and safety information to section 5.10 and waste handling information to section 15.2.

17.3.4 Changed the preparation of sodium sulfate in sections 7.2.7, 7.3.8, 7.5.6, 7.6.1.

17.3.5 Changed the oven temperature for alumina and silica gel in section 7.6.6 and 7.6.9.

17.4 Summary of revisions to SOP for revision 5.

17.4.1 Added information to sections 3.37, 8.1, 12.1, 13.1, Appendix I.

17.5 Summary of revisions to SOP for revision 4.

17.5.1 Corrected the %D for 13C12-1,2,3,6,7,8-HxCDD and –HxCDF for 23 and TO-9A. Updated sections 5 and 15 to meet corporate EH&S requirements.

17.6 Summary of modifications to SOP for revision 3.

17.6.1 Incorporated all PCDD/PCDF analysis methods including 8290, 23, 0023A, and TO-9A into this method.

17.6.2 Revised all Tables to reflect requirements for each analysis method.

17.6.3 Removed instruction to follow carbon cleanup with silica gel/alumina cleanup.

17.6.4 Modified the solids determination procedure in section 11.3.6.4 from that specified by method 1613B.

17.7 List of tables and figures referenced in the body of the SOP.

17.7.1 Table 1 – Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

17.7.2 Table 2 – Methods – All, Minimum Levels by Matrix

17.7.3 Table 3 – Methods – 1613B and 8290, Retention Time References, Quantitation References, and Relative Retention Times

17.7.4 Table 4 – Methods – 23, 0023A, and TO-9A, Retention Time References and Quantitation References.

17.7.5 Table 5 – Methods – 1613B and 8290, Initial Calibration Standard Concentrations and Acceptance Criteria.

17.7.6 Table 6 – Methods – 23, 0023A, and TO-9A, Initial Calibration Standard Concentrations and Acceptance Criteria.

17.7.7 Table 7 – Methods – 1613B and 8290, Daily Verification Standard (VER) Concentrations and Acceptance Criteria.

17.7.8 Table 8 – Methods – 23, 0023A, and TO-9A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria.

17.7.9 Table 9 – Method – 1613B, Initial Precision and Recovery (IPR) Acceptance Criteria.

17.7.10 Table 10 – Methods – 8290, 23, 0023A, and TO-9A, Initial Precision and Recovery (IPR) Acceptance Criteria.

17.7.11 Table 11 – Laboratory Control Sample (LCS/OPR) Spiking Solution Component Concentrations and Acceptance Limits.

17.7.12 Table 12 – Method – 8290. Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits.

17.7.13 Table 13- Methods – 1613B and 8290, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.7.14 Table 14 – Method – 1613B, Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.7.15 Table 15 – Methods – 23, 0023A, and TO-9A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.7.16 Table 16 – Methods – 23, 0023A, and TO-9A, Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.7.17 Table 17 – Methods – All, Recovery Standard Spiking Solution Component Concentrations.

17.7.18 Table 18 – Rtx-5/DB-5 Column Window Defining Standard Mixture Components.

17.7.19 Table 19 – Rtx-5 (DB-5) Column Performance Standard Mixture Components.

17.7.20 Table 20 – DB-225 (Rtx-225) Column Performance Standard Mixture Components.

17.7.21 Table 21 – Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs.

17.7.22 Table 22 – Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs.

17.7.23 Figure 1 – Recommended GC Operating Conditions.

17.7.24 Figure 2 – Recommended MID Descriptors.

17.7.25 Figure 3 – Example Sample Prep Benchsheet

17.7.26 Figure 4 – Example Data Review Checklist.

17.7.27 Figure 5 – Aqueous sample Extraction Flowchart

17.7.28 Figure 6 – Solid Sample Extraction Flowchart

17.7.29 Figure 7 – Sample Cleanup Flowchart

17.7.30 Figure 8- Analysis of PCDD's and PCDF's by HRGC/HRMS Flowchart.

History of Revisions

HISTORY OF REVISION PAGE

| REV NO. | DATE | PAGES AFFECTED | REASON FOR REVISION |
|---|---|---|---|
| 0 | 02/26/97 | All | Initial version of the SOP |
| 1 | 08/31/99 | All | Procedure review. |
| 2 | 01/28/02 | All | Procedure review. |
| 3 | 04/26/03 | All | Procedure review |
| 4 | 11/12/03 | 56 of 83 | Corrected the %D for $^{13}C_{12}$-1,2,3,6,7,8-HxCDD and –HxCDF for 23 and TO-9A. Updated sections 5 and 15 to meet corporate EH&S requirements. |
| 5 | 6/18/04 | All | Added information to sections 3.37, 8.1, 12.1, 13.1, Appendix I. |
| 6 | 9/27/05 | All | Added an exception to 1613B allowing OCDD over calibration range. Added health and safety information to section 5.10 and waste handling information to section 15.2. Updated reagent preparation information for sodium sulfate, alumina and silica gel. Added RLs for biological tissues in Table 2. |

## Table 1

**Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)**

| PCDD's/PCDF's [1] Isomer/Congener | CAS Registry | Labeled Analog | CAS Registry |
|---|---|---|---|
| 2,3,7,8-TCDD | 1746-01-6 | $^{13}C_{12}$-2,3,7,8-TCDD | 76523-40-5 |
| | | $^{37}Cl_4$-2,3,7,8-TCDD | 85508-50-5 |
| Total TCDD | 41903-57-5 | | |
| 2,3,7,8-TCDF | 51207-31-9 | $^{13}C_{12}$-2,3,7,8-TCDF | 89059-46-1 |
| Total TCDF | 55722-27-5 | | |
| 1,2,3,7,8-PeCDD | 40321-76-4 | $^{13}C_{12}$-1,2,3,7,8-PeCDD | 109719-79-1 |
| Total PeCDD | 36088-22-9 | | |
| 1,2,3,7,8-PeCDF | 57117-41-6 | $^{13}C_{12}$-1,2,3,7,8-PeCDF | 109719-77-9 |
| 2,3,4,7,8-PeCDF | 57117-31-4 | $^{13}C_{12}$-2,3,4,7,8-PeCDF | 116843-02-8 |
| Total PeCDF | 30402-15-4 | | |
| 1,2,3,4,7,8-HxCDD | 39227-28-6 | $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 109719-80-4 |
| 1,2,3,6,7,8-HxCDD | 57653-85-7 | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 109719-81-5 |
| 1,2,3,7,8,9-HxCDD | 19408-74-3 | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 109719-82-6 |
| Total HxCDD | 34465-46-8 | | |
| 1,2,3,4,7,8-HxCDF | 70648-26-9 | $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 114423-98-2 |
| 1,2,3,6,7,8-HxCDF | 57117-44-9 | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 116843-03-9 |
| 2,3,4,6,7,8-HxCDF | 60851-34-5 | $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 116843-05-1 |
| 1,2,3,7,8,9-HxCDF | 72918-21-9 | $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 116843-04-0 |
| Total HxCDF | 55684-94-1 | | |
| 1,2,3,4,6,7,8-HpCDD | 35822-46-9 | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 109719-83-7 |
| Total HpCDD | 37871-00-4 | | |
| 1,2,3,4,6,7,8-HpCDF | 67562-39-4 | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 109719-84-8 |
| 1,2,3,4,7,8,9-HpCDF | 55673-89-7 | $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 109719-94-0 |
| Total HpCDF | 38998-75-3 | | |
| OCDD | 3268-87-9 | $^{13}C_{12}$-OCDD | 114423-97-1 |
| OCDF | 39001-02-0 | none | |

**Notes:**

1. Polychlorinated dioxins and furans

| | | | |
|---|---|---|---|
| TCDD | = Tetrachlorodibenzo-p-dioxin | TCDF | = Tetrachlorodibenzofuran |
| PeCDD | = Pentachlorodibenzo-p-dioxin | PeCDF | = Pentachlorodibenzofuran |
| HxCDD | = Hexachlorodibenzo-p-dioxin | HxCDF | = Hexachlorodibenzofuran |
| HpCDD | = Heptachlorodibenzo-p-dioxin | HpCDF | = Heptachlorodibenzofuran |
| OCDD | = Octachlorodibenzo-p-dioxin | OCDF | = Octachlorodibenzofuran |

## Table 2

### Methods – All
### Minimum Levels by Matrix

| Analyte | Extract (ng/mL)[1] | Water (pg/L)[2] | Solids (pg/g)[3] | Biological Tissue (pg/g)[3] | Waste (pg/g)[4] | Air/Wipe (pg)[5] |
|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 0.5 | 10 | 1 | 1 | 10 | 10 |
| 2,3,7,8-TCDF | 0.5 | 10 | 1 | 1 | 10 | 10 |
| 1,2,3,7,8-PeCDD | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,7,8-PeCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 2,3,4,7,8-PeCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,4,7,8-HxCDD | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,6,7,8-HxCDD | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,7,8,9-HxCDD | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,4,7,8-HxCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,6,7,8-HxCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 2,3,4,6,7,8-HxCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,7,8,9-HxCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,4,6,7,8-HpCDD | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,4,6,7,8-HpCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| 1,2,3,4,7,8,9-HpCDF | 2.5 | 50 | 5 | 5 | 50 | 50 |
| OCDD | 5.0 | 100 | 10 | 10 | 100 | 100 |
| OCDF | 5.0 | 100 | 10 | 10 | 100 | 100 |

**Notes:**

1 Concentration in the extract assuming a 20 µL volume.
2 Based on a sample volume of 1.0 L.
3 Based on a sample volume of 10.0 g.
4 Based on a sample volume of 1.0g.
5 Based on extraction of the entire sample.

## Table 3

### Methods – 1613B and 8290
### Retention Time References, Quantitation References, and Relative Retention Times

| Analyte | Retention Time and Quantitation Reference | Relative Retention Time |
|---|---|---|
| *Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard* | | |
| 2,3,7,8-TCDD | $^{13}C_{12}$-2,3,7,8-TCDD | 0.999-1.002 |
| 2,3,7,8-TCDF | $^{13}C_{12}$-2,3,7,8-TCDF | 0.999-1.003 |
| 1,2,3,7,8-PeCDD | $^{13}C_{12}$-1,2,3,7,8-PeCDD | 0.999-1.002 |
| 1,2,3,7,8-PeCDF | $^{13}C_{12}$-1,2,3,7,8-PeCDF | 0.999-1.002 |
| 2,3,4,7,8-PeCDF | $^{13}C_{12}$-2,3,4,7,8-PeCDF | 0.999-1.002 |
| $^{13}C_{12}$-2,3,7,8-TCDD | $^{13}C_{12}$-1,2,3,4-TCDD | 0.976-1.043 |
| $^{37}Cl_4$-2,3,7,8-TCDD | $^{13}C_{12}$-1,2,3,4-TCDD | 0.989-1.052 |
| $^{13}C_{12}$-2,3,7,8-TCDF | $^{13}C_{12}$-1,2,3,4-TCDD | 0.923-1.103 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | $^{13}C_{12}$-1,2,3,4-TCDD | 1.000-1.567 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | $^{13}C_{12}$-1,2,3,4-TCDD | 1.000-1.425 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | $^{13}C_{12}$-1,2,3,4-TCDD | 1.011-1.526 |
| *Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard* | | |
| 1,2,3,4,7,8-HxCDD | $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 0.999-1.001 |
| 1,2,3,6,7,8-HxCDD | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 0.998-1.004 |
| 1,2,3,7,8,9-HxCDD | --[1] | 1.000-1.019 |
| 1,2,3,4,7,8-HxCDF | $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 0.999-1.001 |
| 1,2,3,6,7,8-HxCDF | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 0.997-1.005 |
| 2,3,4,6,7,8-HxCDF | $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 0.999-1.001 |
| 1,2,3,7,8,9-HxCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 0.999-1.001 |
| 1,2,3,4,6,7,8-HpCDD | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 0.999-1.001 |
| 1,2,3,4,6,7,8-HpCDF | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 0.999-1.001 |
| 1,2,3,4,7,8,9-HpCDF | $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 0.999-1.001 |
| OCDD | $^{13}C_{12}$-OCDD | 0.999-1.001 |
| OCDF | $^{13}C_{12}$-OCDD | 0.999-1.008 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.977-1.000 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.981-1.003 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.944-0.970 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.949-0.975 |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.959-1.021 |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.977-1.047 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 1.086-1.110 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 1.043-1.085 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 1.057-1.151 |
| $^{13}C_{12}$-OCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 1.032-1.311 |

**Notes:**

1 The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

## Table 4

### Methods – 23, 0023A, and TO-9A
### Retention Time References and Quantitation References

| Analyte | Retention Time and Quantitation Reference |
|---|---|
| *Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard* | |
| 2,3,7,8-TCDD | $^{13}C_{12}$-2,3,7,8-TCDD |
| 2,3,7,8-TCDF | $^{13}C_{12}$-2,3,7,8-TCDF |
| 1,2,3,7,8-PeCDD | $^{13}C_{12}$-1,2,3,7,8-PeCDD |
| 1,2,3,7,8-PeCDF | $^{13}C_{12}$-1,2,3,7,8-PeCDF |
| 2,3,4,7,8-PeCDF | $^{13}C_{12}$-1,2,3,7,8-PeCDF |
| $^{13}C_{12}$-2,3,7,8-TCDD | $^{13}C_{12}$-1,2,3,4-TCDD |
| $^{37}Cl_4$-2,3,7,8-TCDD | $^{13}C_{12}$-2,3,7,8-TCDD |
| $^{13}C_{12}$-2,3,7,8-TCDF | $^{13}C_{12}$-1,2,3,4-TCDD |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | $^{13}C_{12}$-1,2,3,4-TCDD |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | $^{13}C_{12}$-1,2,3,4-TCDD |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | $^{13}C_{12}$-1,2,3,7,8-PeCDF |
| *Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard* | |
| 1,2,3,4,7,8-HxCDD | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD |
| 1,2,3,6,7,8-HxCDD | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD |
| 1,2,3,7,8,9-HxCDD | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD |
| 1,2,3,4,7,8-HxCDF | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF |
| 1,2,3,6,7,8-HxCDF | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF |
| 2,3,4,6,7,8-HxCDF | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF |
| 1,2,3,7,8,9-HxCDF | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF |
| 1,2,3,4,6,7,8-HpCDD | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD |
| 1,2,3,4,6,7,8-HpCDF | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF |
| 1,2,3,4,7,8,9-HpCDF | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF |
| OCDD | $^{13}C_{12}$-OCDD |
| OCDF | $^{13}C_{12}$-OCDD |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | $^{13}C_{12}$-1,2,3,6,7,8-HxCDD |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | $^{13}C_{12}$-1,2,3,6,7,8-HxCDF |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF |
| $^{13}C_{12}$-OCDD | $^{13}C_{12}$-1,2,3,7,8,9-HxCDD |

## Table 5

### Methods – 1613B and 8290
### Initial Calibration Standard Concentrations and Acceptance Criteria

| Analyte | CS1 (ng/mL) | CS2 (ng/mL) | CS3 (ng/mL) | CS4 (ng/mL) | CS5 (ng/mL) | 1613B %RSD | 8290 %RSD |
|---|---|---|---|---|---|---|---|
| **Native PCDD's and PCDF's** | | | | | | | |
| 2,3,7,8-TCDD | 0.5 | 2.0 | 10 | 40 | 200 | ±20 | ±20 |
| 2,3,7,8-TCDF | 0.5 | 2.0 | 10 | 40 | 200 | ±20 | ±20 |
| 1,2,3,7,8-PeCDD | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,7,8-PeCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 2,3,4,7,8-PeCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,4,7,8-HxCDD | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,6,7,8-HxCDD | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,7,8,9-HxCDD | 2.5 | 10 | 50 | 200 | 1000 | ±35 | ±20 |
| 1,2,3,4,7,8-HxCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,6,7,8-HxCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 2,3,4,6,7,8-HxCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,7,8,9-HxCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,4,6,7,8-HpCDD | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,4,6,7,8-HpCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| 1,2,3,4,7,8,9-HpCDF | 2.5 | 10 | 50 | 200 | 1000 | ±20 | ±20 |
| OCDD | 5.0 | 20 | 100 | 400 | 2000 | ±20 | ±20 |
| OCDF | 5.0 | 20 | 100 | 400 | 2000 | ±35 | ±20 |
| **Labeled Internal Standards** | | | | | | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 100 | 100 | 100 | 100 | 100 | ±35 | ±30 |
| $^{13}C_{12}$-OCDD | 200 | 200 | 200 | 200 | 200 | ±35 | ±30 |
| **Labeled Cleanup Standard** | | | | | | | |
| $^{37}Cl_4$-2,3,7,8-TCDD | 0.5 | 2.0 | 10 | 40 | 200 | ±35 | ±30 |
| **Labeled Recovery Standard** | | | | | | | |
| $^{13}C_{12}$-1,2,3,4-TCDD | 100 | 100 | 100 | 100 | 100 | - | - |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 100 | 100 | 100 | 100 | 100 | - | - |

## Table 6

### Methods – 23, 0023A, and TO-9A
### Initial Calibration Standard Concentrations and Acceptance Criteria

| Analyte | CS1 (ng/mL) | CS2 (ng/mL) | CS3 (ng/mL) | CS4 (ng/mL) | CS5 (ng/mL) | 23 / TO-9A %RSD | 0023A %RSD |
|---|---|---|---|---|---|---|---|
| **Native PCDD's and PCDF's** | | | | | | | |
| 2,3,7,8-TCDD | 0.5 | 1.0 | 5 | 50 | 100 | ±25 | ±20 |
| 2,3,7,8-TCDF | 0.5 | 1.0 | 5 | 50 | 100 | ±25 | ±20 |
| 1,2,3,7,8-PeCDD | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,7,8-PeCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 2,3,4,7,8-PeCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,4,7,8-HxCDD | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,6,7,8-HxCDD | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,7,8,9-HxCDD | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,4,7,8-HxCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,6,7,8-HxCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 2,3,4,6,7,8-HxCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,7,8,9-HxCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,4,6,7,8-HpCDD | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,4,6,7,8-HpCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| 1,2,3,4,7,8,9-HpCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±20 |
| OCDD | 5.0 | 10 | 50 | 500 | 1000 | ±25 | ±20 |
| OCDF | 5.0 | 10 | 50 | 500 | 1000 | ±30 | ±20 |
| **Labeled Internal Standards** | | | | | | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 100 | 100 | 100 | 100 | 100 | ±25 | ±30 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 100 | 100 | 100 | 100 | 100 | ±30 | ±30 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 100 | 100 | 100 | 100 | 100 | ±30 | ±30 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 100 | 100 | 100 | 100 | 100 | ±30 | ±30 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 100 | 100 | 100 | 100 | 100 | ±25 | ±30 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 100 | 100 | 100 | 100 | 100 | ±30 | ±30 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 100 | 100 | 100 | 100 | 100 | ±30 | ±30 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 100 | 100 | 100 | 100 | 100 | ±30 | ±30 |
| $^{13}C_{12}$-OCDD | 200 | 200 | 200 | 200 | 200 | ±30 | ±30 |
| **Surrogate Standards** | | | | | | | |
| $^{37}Cl_4$-2,3,7,8-TCDD | 0.5 | 1.0 | 5 | 50 | 100 | ±25 | ±30 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±30 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±30 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±30 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 2.5 | 5 | 25 | 250 | 500 | ±25 | ±30 |
| **Labeled Recovery Standard** | | | | | | | |
| $^{13}C_{12}$-1,2,3,4-TCDD | 100 | 100 | 100 | 100 | 100 | - | - |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 100 | 100 | 100 | 100 | 100 | - | - |

## Table 7

### Methods – 1613B and 8290
### Daily Verification Standard (VER) Concentrations and Acceptance Criteria

| Analyte | VER (ng/mL) | 1613B All Isomers (ng/mL) | 1613B Tetra only (ng/mL) | 8290 Shift Open %D | 8290 Shift Close[1] %D |
|---|---|---|---|---|---|
| **Native PCDD's and PCDF's** | | | | | |
| 2,3,7,8-TCDD | 10 | 7.8-12.9 | 8.2-12.3 | ±20 | ±25 |
| 2,3,7,8-TCDF | 10 | 8.4-12.0 | 8.6-11.6 | ±20 | ±25 |
| 1,2,3,7,8-PeCDD | 50 | 39-65 | - | ±20 | ±25 |
| 1,2,3,7,8-PeCDF | 50 | 41-60 | - | ±20 | ±25 |
| 2,3,4,7,8-PeCDF | 50 | 41-61 | - | ±20 | ±25 |
| 1,2,3,4,7,8-HxCDD | 50 | 39-64 | - | ±20 | ±25 |
| 1,2,3,6,7,8-HxCDD | 50 | 39-64 | - | ±20 | ±25 |
| 1,2,3,7,8,9-HxCDD | 50 | 41-61 | - | ±20 | ±25 |
| 1,2,3,4,7,8-HxCDF | 50 | 45-56 | - | ±20 | ±25 |
| 1,2,3,6,7,8-HxCDF | 50 | 44-57 | - | ±20 | ±25 |
| 2,3,4,6,7,8-HxCDF | 50 | 44-57 | - | ±20 | ±25 |
| 1,2,3,7,8,9-HxCDF | 50 | 45-56 | - | ±20 | ±25 |
| 1,2,3,4,6,7,8-HpCDD | 50 | 43-58 | - | ±20 | ±25 |
| 1,2,3,4,6,7,8-HpCDF | 50 | 45-55 | - | ±20 | ±25 |
| 1,2,3,4,7,8,9-HpCDF | 50 | 43-58 | - | ±20 | ±25 |
| OCDD | 100 | 79-126 | - | ±20 | ±25 |
| OCDF | 100 | 63-159 | - | ±20 | ±25 |
| **Labeled Internal Standards** | | | | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 100 | 82-121 | 85-117 | ±30 | ±35 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 100 | 71-140 | 76-131 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 100 | 62-160 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 100 | 76-130 | - | ±30 | ±35 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 100 | 77-130 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 100 | 85-117 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 100 | 85-118 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 100 | 76-131 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 100 | 70-143 | - | ±30 | ±35 |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 100 | 73-137 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 100 | 74-135 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 100 | 72-138 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 100 | 78-129 | - | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 100 | 77-129 | - | ±30 | ±35 |
| $^{13}C_{12}$-OCDD | 200 | 96-415 | - | ±30 | ±35 |
| **Labeled Cleanup Standard** | | | | | |
| $^{37}Cl_4$-2,3,7,8-TCDD | 10 | 7.9-12.7 | 8.3-12.1 | ±30 | ±35 |
| **Labeled Recovery Standard** | | | | | |
| $^{13}C_{12}$-1,2,3,4-TCDD | 100 | - | - | - | - |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 100 | - | - | - | - |

**Notes:**

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

## Table 8

## Methods – 23, 0023A, and TO-9A
## Daily Verification Standard (VER) Concentrations and Acceptance Criteria

| Analyte | VER (ng/mL) | 23 and TO-9A %D | 0023A Shift Open %D | 0023A Shift Close[1] %D |
|---|---|---|---|---|
| **Native PCDD's and PCDF's** | | | | |
| 2,3,7,8-TCDD | 5 | ±25 | ±20 | ±25 |
| 2,3,7,8-TCDF | 5 | ±25 | ±20 | ±25 |
| 1,2,3,7,8-PeCDD | 25 | ±25 | ±20 | ±25 |
| 1,2,3,7,8-PeCDF | 25 | ±25 | ±20 | ±25 |
| 2,3,4,7,8-PeCDF | 25 | ±25 | ±20 | ±25 |
| 1,2,3,4,7,8-HxCDD | 25 | ±25 | ±20 | ±25 |
| 1,2,3,6,7,8-HxCDD | 25 | ±25 | ±20 | ±25 |
| 1,2,3,7,8,9-HxCDD | 25 | ±25 | ±20 | ±25 |
| 1,2,3,4,7,8-HxCDF | 25 | ±25 | ±20 | ±25 |
| 1,2,3,6,7,8-HxCDF | 25 | ±25 | ±20 | ±25 |
| 2,3,4,6,7,8-HxCDF | 25 | ±25 | ±20 | ±25 |
| 1,2,3,7,8,9-HxCDF | 25 | ±25 | ±20 | ±25 |
| 1,2,3,4,6,7,8-HpCDD | 25 | ±25 | ±20 | ±25 |
| 1,2,3,4,6,7,8-HpCDF | 25 | ±25 | ±20 | ±25 |
| 1,2,3,4,7,8,9-HpCDF | 25 | ±25 | ±20 | ±25 |
| OCDD | 50 | ±25 | ±20 | ±25 |
| OCDF | 50 | ±30 | ±20 | ±25 |
| **Labeled Internal Standards** | | | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 100 | ±25 | ±30 | ±35 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 100 | ±30 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 100 | ±30 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 100 | ±30 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 100 | ±25 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 100 | ±30 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 100 | ±30 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 100 | ±30 | ±30 | ±35 |
| $^{13}C_{12}$-OCDD | 200 | ±30 | ±30 | ±35 |
| **Surrogate Standards** | | | | |
| $^{37}Cl_4$-2,3,7,8-TCDD | 5 | ±25 | ±30 | ±35 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 25 | ±25 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 25 | ±25 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 25 | ±25 | ±30 | ±35 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 25 | ±25 | ±30 | ±35 |
| **Labeled Recovery Standard** | | | | |
| $^{13}C_{12}$-1,2,3,4-TCDD | 100 | - | - | |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 100 | - | - | |

**Notes:**

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

## Table 9

## Method – 1613B
## Initial Precision and Recovery (IPR) Acceptance Criteria

| Analyte | Test Conc. (ng/mL)[1] | 1613B $s^2$ (ng/mL)[1] | 1613B $X^3$ (ng/ml)[1] | 1613B Tetra Only $s^2$ (ng/mL)[1] | 1613B Tetra Only $X^3$ (ng/ml)[1] |
|---|---|---|---|---|---|
| **Native PCDD's and PCDF's** | | | | | |
| 2,3,7,8-TCDD | 10 | 2.8 | 8.3-12.9 | 2.7 | 8.7-12.4 |
| 2,3,7,8-TCDF | 10 | 2.0 | 8.7-13.7 | 2.0 | 9.1-13.1 |
| 1,2,3,7,8-PeCDD | 50 | 7.5 | 38-66 | - | - |
| 1,2,3,7,8-PeCDF | 50 | 7.5 | 43-62 | - | - |
| 2,3,4,7,8-PeCDF | 50 | 8.6 | 36-75 | - | - |
| 1,2,3,4,7,8-HxCDD | 50 | 9.4 | 39-76 | - | - |
| 1,2,3,6,7,8-HxCDD | 50 | 7.7 | 42-62 | - | - |
| 1,2,3,7,8,9-HxCDD | 50 | 11.1 | 37-71 | - | - |
| 1,2,3,4,7,8-HxCDF | 50 | 8.7 | 41-59 | - | - |
| 1,2,3,6,7,8-HxCDF | 50 | 6.7 | 46-60 | - | - |
| 2,3,4,6,7,8-HxCDF | 50 | 7.4 | 37-74 | - | - |
| 1,2,3,7,8,9-HxCDF | 50 | 6.4 | 42-61 | - | - |
| 1,2,3,4,6,7,8-HpCDD | 50 | 7.7 | 38-65 | - | - |
| 1,2,3,4,6,7,8-HpCDF | 50 | 6.3 | 45-56 | - | - |
| 1,2,3,4,7,8,9-HpCDF | 50 | 8.1 | 43-63 | - | - |
| OCDD | 100 | 19 | 89-127 | - | - |
| OCDF | 100 | 27 | 74-146 | - | - |
| **Labeled Internal Standards** | | | | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 50 | 18.5 | 14-67 | 17.5 | 16-57.5 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 50 | 17.5 | 15.5-56.5 | 17 | 17.5-49.5 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 50 | 19.5 | 13.5-92 | - | - |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 50 | 17.0 | 13.5-78 | - | - |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 50 | 19.0 | 8-139.5 | - | - |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 50 | 20.5 | 14.5-73.5 | - | - |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 50 | 19.0 | 17-61 | - | - |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 50 | 21.5 | 13.5-76 | - | - |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 50 | 17.5 | 15-61 | - | - |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 50 | 18.5 | 14.5-68 | - | - |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 50 | 20.0 | 12-78.5 | - | - |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 50 | 17.5 | 17-64.5 | - | - |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 50 | 20.5 | 16-55 | - | - |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 50 | 20.0 | 14-70.5 | - | - |
| $^{13}C_{12}$-OCDD | 100 | 47.5 | 20.5-138 | - | - |
| **Labeled Cleanup Standard** | | | | | |
| $^{37}Cl_4$-2,3,7,8-TCDD | 10 | 3.6 | 3.9-15.4 | 3.4 | 4.5-13.4 |

**Notes:**

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the concentration

3 X = average concentration. The acceptance range for average recovery may be normalized (shifted to center on 100% recovery) to compensate for the bias in the collaborative study used to develop the acceptance criteria.

## Table 10

### Methods – 8290, 23, 0023A, and TO-9A
### Initial Precision and Recovery (IPR) Acceptance Criteria

| Analyte | Test Conc (ng/mL)[1] | s[2] (%Rec) | X[3] (%Rec) |
|---|---|---|---|
| **Native PCDD's and PCDF's** | | | |
| 2,3,7,8-TCDD | 10 | 15[4] | 70-130[4] |
| 2,3,7,8-TCDF | 10 | 15[4] | 70-130[4] |
| 1,2,3,7,8-PeCDD | 50 | 15[4] | 70-130[4] |
| 1,2,3,7,8-PeCDF | 50 | 15[4] | 70-130[4] |
| 2,3,4,7,8-PeCDF | 50 | 15[4] | 70-130[4] |
| 1,2,3,4,7,8-HxCDD | 50 | 15[4] | 70-130[4] |
| 1,2,3,6,7,8-HxCDD | 50 | 15[4] | 70-130[4] |
| 1,2,3,7,8,9-HxCDD | 50 | 15[4] | 70-130[4] |
| 1,2,3,4,7,8-HxCDF | 50 | 15[4] | 70-130[4] |
| 1,2,3,6,7,8-HxCDF | 50 | 15[4] | 70-130[4] |
| 2,3,4,6,7,8-HxCDF | 50 | 15[4] | 70-130[4] |
| 1,2,3,7,8,9-HxCDF | 50 | 15[4] | 70-130[4] |
| 1,2,3,4,6,7,8-HpCDD | 50 | 15[4] | 70-130[4] |
| 1,2,3,4,6,7,8-HpCDF | 50 | 15[4] | 70-130[4] |
| 1,2,3,4,7,8,9-HpCDF | 50 | 15[4] | 70-130[4] |
| OCDD | 100 | 15[4] | 70-130[4] |
| OCDF | 100 | 15[4] | 70-130[4] |

**Notes:**

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the percent recovery

3 X = average percent recovery

4 In-house generated historical control-limits may be used in place of the specified limit.

## Table 11

## Laboratory Control Sample (LCS/OPR) Spiking Solution Component Concentrations and Acceptance Limits

| Analyte | LCS Solution Conc. (ng/mL)[1] | Final Extract Conc (ng/mL)[2] | 1613B OPR Conc (ng/mL)[2] | 8290, 23, 0023A, TO-9A Recovery (%Rec) |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 0.2 | 10 | 6.7-15.8 | 70-130[4] |
| 2,3,7,8-TCDF | 0.2 | 10 | 7.5-15.8 | 70-130[4] |
| 1,2,3,7,8-PeCDD | 1.0 | 50 | 35-71 | 70-130[4] |
| 1,2,3,7,8-PeCDF | 1.0 | 50 | 40-67 | 70-130[4] |
| 2,3,4,7,8-PeCDF | 1.0 | 50 | 34-80 | 70-130[4] |
| 1,2,3,4,7,8-HxCDD | 1.0 | 50 | 35-82 | 70-130[4] |
| 1,2,3,6,7,8-HxCDD | 1.0 | 50 | 38-67 | 70-130[4] |
| 1,2,3,7,8,9-HxCDD | 1.0 | 50 | 32-81 | 70-130[4] |
| 1,2,3,4,7,8-HxCDF | 1.0 | 50 | 36-67 | 70-130[4] |
| 1,2,3,6,7,8-HxCDF | 1.0 | 50 | 42-65 | 70-130[4] |
| 2,3,4,6,7,8-HxCDF | 1.0 | 50 | 35-78 | 70-130[4] |
| 1,2,3,7,8,9-HxCDF | 1.0 | 50 | 39-65 | 70-130[4] |
| 1,2,3,4,6,7,8-HpCDD | 1.0 | 50 | 35-70 | 70-130[4] |
| 1,2,3,4,6,7,8-HpCDF | 1.0 | 50 | 41-61 | 70-130[4] |
| 1,2,3,4,7,8,9-HpCDF | 1.0 | 50 | 39-69 | 70-130[4] |
| OCDD | 2.0 | 100 | 78-144 | 70-130[4] |
| OCDF | 2.0 | 100 | 63-170 | 70-130[4] |
| **Tetras Only** | | | | |
| 2,3,7,8-TCDD | 0.2 | 10 | 7.3-14.6 | 70-130[4] |
| 2,3,7,8-TCDF | 0.2 | 10 | 8.0-14.7 | 70-130[4] |

**Notes:**

1 1.0 mL of this solution is added to the OPR sample before extraction (see section 7.11.1).

2 The final extract concentration is based on an extract volume of 20-µL.

3 Spike concentrations are based on a 1.0 L extraction for Water, 10.0g extraction for Solids, and entire sample extraction for Air/Wipe samples.

4 In-house generated historical control-limits may be used in place of the specified limit.

## Table 12

## Method - 8290
## Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits[1]

| Analyte | LCS Solution Conc. (ng/mL)[2] | Final Extract Conc (ng/mL)[3] | 8290 Recovery (%Rec) | 8290 Precision (RPD) |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 0.2 | 10 | 70-130[4] | ±15[4] |
| 2,3,7,8-TCDF | 0.2 | 10 | 70-130[4] | ±15[4] |
| 1,2,3,7,8-PeCDD | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,7,8-PeCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 2,3,4,7,8-PeCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,4,7,8-HxCDD | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,6,7,8-HxCDD | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,7,8,9-HxCDD | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,4,7,8-HxCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,6,7,8-HxCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 2,3,4,6,7,8-HxCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,7,8,9-HxCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,4,6,7,8-HpCDD | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,4,6,7,8-HpCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| 1,2,3,4,7,8,9-HpCDF | 1.0 | 50 | 70-130[4] | ±15[4] |
| OCDD | 2.0 | 100 | 70-130[4] | ±15[4] |
| OCDF | 2.0 | 100 | 70-130[4] | ±15[4] |

Notes:

1 If insufficient sample exists for MS/MSD analysis, these limits apply to LCS/LCSD samples.
2 mL of this solution is added to the OPR sample before extraction (see section 7.11.2).
3 The final extract concentration is based on an extract volume of 20-µL.
4 In-house generated historical control-limits may be used in place of the specified limit.

## Table 13

### Methods – 1613B and 8290
### Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

| Labeled Analyte | Solution Conc (ng/mL)[1] | Test Conc. (ng/mL)[2] | 1613B OPR Conc (ng/mL)[2] | 1613B Sample Conc (ng/mL)[2] | 8290 Recovery (%Rec) |
|---|---|---|---|---|---|
| $^{13}C_{12}$-2,3,7,8-TCDD | 1.0 | 50 | 10.0-87.5 | 12.5-82.0 | 40-135 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 1.0 | 50 | 11.0-76.0 | 12.0-84.5 | 40-135 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 1.0 | 50 | 10.5-113.5 | 12.5-90.5 | 40-135 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 1.0 | 50 | 10.5-96.0 | 12.0-92.5 | 40-135 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 1.0 | 50 | 6.5-164.0 | 10.5-89.0 | 40-135 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 1.0 | 50 | 10.5-96.5 | 16.0-70.5 | 40-135 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 1.0 | 50 | 12.5-81.5 | 14.0-65.0 | 40-135 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 1.0 | 50 | 9.5-101.0 | 13.0-76.0 | 40-135 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 1.0 | 50 | 10.5-79.5 | 13.0-61.5 | 40-135 |
| $^{13}C_{12}$-2,3,4,6,7,8-HxCDF | 1.0 | 50 | 11.0-88.0 | 14.0-68.0 | 40-135 |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDF | 1.0 | 50 | 8.5-102.5 | 14.5-73.5 | 40-135 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 1.0 | 50 | 13.0-83.0 | 11.5-70.0 | 40-135 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 1.0 | 50 | 10.5-79.0 | 14.0-71.5 | 40-135 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 1.0 | 50 | 10.0-93.0 | 13.0-69.0 | 40-135 |
| $^{13}C_{12}$-OCDD | 2.0 | 100 | 13.0-198.5 | 17.0-157 | 40-135 |
| Tetras Only | | | | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 1.0 | 50 | 12.5-70.5 | 15.5-68.5 | 40-135 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 1.0 | 50 | 13.0-63.0 | 14.5-70.0 | 40-135 |

Notes:
1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to extraction (see section 7.11.3).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

## Table 14

### Method – 1613B
### Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

| Labeled Analyte | Solution Conc (ng/mL)[1] | Test Conc. (ng/mL)[2] | 1613B OPR Conc (ng/mL)[2] | 1613B Sample Conc (ng/mL)[2] | 1613B OPR Tetra Only Conc (ng/mL)[2] | 1613B Sample Tetra Only Conc (ng/mL)[2] |
|---|---|---|---|---|---|---|
| $^{37}Cl_4$-2,3,7,8-TCDD | 0.2 | 10 | 3.1-19.1 | 3.5-19.7 | 3.7-15.8 | 4.2-16.4 |

Notes:
1 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to cleanup (see section 7.11.4).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

## Table 15

### Methods – 23, 0023A, and TO-9A
### Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

| Labeled Analyte | Solution Conc (ng/mL)[1] | Test Conc. (ng/mL)[2] | 23 Recovery (%Rec) | 0023A Recovery (%Rec) | TO-9A Recovery (%Rec) |
|---|---|---|---|---|---|
| $^{13}C_{12}$-2,3,7,8-TCDD | 1.0 | 50 | 40-130 | 40-135 | 50-120 |
| $^{13}C_{12}$-2,3,7,8-TCDF | 1.0 | 50 | 40-130 | 40-135 | 50-120 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDD | 1.0 | 50 | 40-130 | 40-135 | 50-120 |
| $^{13}C_{12}$-1,2,3,7,8-PeCDF | 1.0 | 50 | 40-130 | 40-135 | 50-120 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDD | 1.0 | 50 | 40-130 | 40-135 | 50-120 |
| $^{13}C_{12}$-1,2,3,6,7,8-HxCDF | 1.0 | 50 | 40-130 | 40-135 | 50-120 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD | 1.0 | 50 | 25-130 | 40-135 | 40-120 |
| $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF | 1.0 | 50 | 25-130 | 40-135 | 40-120 |
| $^{13}C_{12}$-OCDD | 2.0 | 100 | 25-130 | 40-135 | 40-120 |

**Notes:**

1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to extraction (see section 7.11.3).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

## Table 16

### Methods – 23, 0023A, and TO-9A
### Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

| Labeled Analyte | Solution Conc (ng/mL)[1] | Test Conc. (ng/mL)[2] | 23 Recovery (%Rec) | 0023A Recovery (%Rec) | TO-9A Recovery (%Rec) |
|---|---|---|---|---|---|
| $^{37}Cl_4$-2,3,7,8-TCDD | 20 | 100 | 70-130 | 70-130 | 50-120 |
| $^{13}C_{12}$-2,3,4,7,8-PeCDF | 20 | 100 | 70-130 | 70-130 | 50-120 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDD | 20 | 100 | 70-130 | 70-130 | 50-120 |
| $^{13}C_{12}$-1,2,3,4,7,8-HxCDF | 20 | 100 | 70-130 | 70-130 | 50-120 |
| $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF | 20 | 100 | 70-130 | 70-130 | 40-120 |

**Notes:**

1 100 µL of the Surrogate Standard Spiking Solution is added to each sample train prior to sampling (see section 7.11.5).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

## Table 17

### Methods – All
### Recovery Standard Spiking Solution Component Concentrations

| Labeled Analyte | Solution Conc (µg/mL)[1] | Test Conc. (ng/mL)[2] |
|---|---|---|
| $^{13}C_{12}$-1,2,3,4-TCDD | 0.1 | 100 |
| $^{13}C_{12}$-1,2,3,7,8,9-HxCDD | 0.1 | 100 |

**Notes:**

1 20 µL of the Recovery Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to analysis (see section 7.11.8).

2 Specifications given as concentration in the final extract, assuming a 20-µL volume

## Table 18

### Rtx-5/DB-5 Column Window Defining Standard Mixture Components

| Congener | First Eluted | Last Eluted |
|---|---|---|
| TCDF | 1,3,6,8- | 1,2,8,9- |
| TCDD | 1,3,6,8- | 1,2,8,9- |
| PeCDF | 1,3,4,6,8- | 1,2,3,8,9- |
| PeCDD | 1,2,4,6,8-/ 1,2,4,7,9- | 1,2,3,8,9- |
| HxCDF | 1,2,3,4,6,8- | 1,2,3,4,8,9- |
| HxCDD | 1,2,4,6,7,9-/ 1,2,4,6,8,9- | 1,2,3,4,6,7- |
| HpCDF | 1,2,3,4,6,7,8- | 1,2,3,4,7,8,9- |
| HpCDD | 1,2,3,4,6,7,9- | 1,2,3,4,6,7,8- |

## Table 19

### Rtx-5 (DB-5) Column Performance Standard Mixture Components

| Isomer |
|---|
| 1,2,3,7/1,2,3,8-TCDD |
| 1,2,3,9-TCDD |
| 2,3,7,8-TCDD |

## Table 20

### DB-225 (Rtx-225) Column Performance Standard Mixture Components

| Isomer |
|---|
| 2,3,4,7-TCDF |
| 2,3,7,8-TCDF |
| 1,2,3,9-TCDF |

**Table 21**

**Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs**

| Descriptor | Accurate Mass[1] | Ion ID | Elemental Composition | Analyte |
|---|---|---|---|---|
| 1 | 292.9825 | LOCK | $C_7F_{11}$ | PFK |
| | 303.9016 | M | $C_{12}H_4{}^{35}Cl_4O$ | TCDF |
| | 305.8987 | M+2 | $C_{12}H_4{}^{35}Cl_3{}^{37}ClO$ | TCDF |
| | 315.9419 | M | $^{13}C_{12}H_4{}^{35}Cl_4O$ | TCDF (S) |
| | 317.9389 | M+2 | $^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$ | TCDF (S) |
| | 319.8965 | M | $C_{12}H_4{}^{35}Cl_4O_2$ | TCDD |
| | 321.8936 | M+2 | $C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$ | TCDD |
| | 327.8847 | M | $C_{12}H_4{}^{37}Cl_4O_2$ | TCDD |
| | 331.9368 | M | $^{13}C_{12}H_4{}^{35}Cl_4O_2$ | TCDD (S) |
| | 333.9338 | M+2 | $^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$ | TCDD (S) |
| | 342.9792 | QC | $C_8F_{13}$ | PFK |
| | 375.8364 | M+2 | $C_{12}H_4{}^{35}Cl_5{}^{37}ClO$ | HxCDPE |
| 2 | 330.9792 | LOCK | $C_7F_{13}$ | PFK |
| | 339.8597 | M+2 | $C_{12}H_3{}^{35}Cl_4{}^{37}ClO$ | PeCDF |
| | 341.8567 | M+4 | $C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$ | PeCDF |
| | 351.9000 | M+2 | $^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$ | PeCDF (S) |
| | 353.8970 | M+4 | $^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$ | PeCDF (S) |
| | 355.8546 | M+2 | $C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$ | PeCDD |
| | 357.8516 | M+4 | $C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$ | PeCDD |
| | 367.8949 | M+2 | $^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$ | PeCDD (S) |
| | 369.8919 | M+4 | $^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$ | PeCDD (S) |
| | 380.9760 | QC | $C_8F_{15}$ | PFK |
| | 409.7974 | M+2 | $C_{12}H_3{}^{35}Cl_6{}^{37}ClO$ | HpCDPE |
| 3 | 373.8208 | M+2 | $C_{12}H_2{}^{35}Cl_5{}^{37}ClO$ | HxCDF |
| | 375.8178 | M+4 | $C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$ | HxCDF |
| | 380.9760 | LOCK | $C_8F_{15}$ | PFK |
| | 383.8639 | M | $^{13}C_{12}H_2{}^{35}Cl_6O$ | HxCDF (S) |
| | 385.8610 | M+2 | $^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$ | HxCDF (S) |
| | 389.8156 | M+2 | $C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$ | HxCDD |
| | 391.8127 | M+4 | $C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$ | HxCDD |
| | 401.8559 | M+2 | $^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$ | HxCDD (S) |
| | 403.8529 | M+4 | $^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$ | HxCDD (S) |
| | 404.9760 | QC | $C_{10}F_{15}$ | PFK |
| | 445.7555 | M+4 | $C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$ | OCDPE |

**Table 21 Continued**

**Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs**

| Descriptor | Accurate Mass[1] | Ion ID | Elemental Composition | Analyte |
|---|---|---|---|---|
| 4 | 404.9760 | LOCK | $C_{10}F_{15}$ | PFK |
| | 407.7818 | M+2 | $C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$ | HpCDF |
| | 409.7788 | M+4 | $C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0$ | HpCDF |
| | 417.8250 | M | $^{13}C_{12}H\ ^{35}Cl_7\ 0$ | HpCDF (S) |
| | 419.8220 | M+2 | $^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$ | HpCDF (S) |
| | 423.7767 | M+2 | $C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$ | HpCDD |
| | 425.7737 | M+4 | $C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$ | HpCDD |
| | 435.8169 | M+2 | $^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$ | HpCDD (S) |
| | 437.8140 | M+4 | $^{13}C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$ | HpCDD (S) |
| | 442.9728 | QC | $C_{10}F_{17}$ | PFK |
| | 479.7165 | M+4 | $C_{12}H\ ^{35}Cl_7\ ^{37}Cl_2\ 0$ | NCDPE |
| 5 | 430.9728 | LOCK | $C_9F_{17}$ | PFK |
| | 441.7428 | M+2 | $C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0$ | OCDF |
| | 443.7399 | M+4 | $C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0$ | OCDF |
| | 457.7377 | M+2 | $C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$ | OCDD |
| | 459.7348 | M+4 | $C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$ | OCDD |
| | 469.7780 | M+2 | $^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$ | OCDD (S) |
| | 471.7750 | M+4 | $^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$ | OCDD (S) |
| | 480.9696 | QC | $C_{10}F_{19}$ | PFK |
| | 513.6775 | M+4 | $C_{12}\ ^{35}Cl_8\ ^{37}Cl_2\ 0$ | DCDPE |

**Notes:**

1 Nuclidic masses used:

| | | | |
|---|---|---|---|
| H = 1.007825 | C = 12.00000 | $^{13}C$ = 13.003355 | F = 18.9984 |
| O = 15.994915 | $^{35}Cl$ = 34.968853 | $^{37}Cl$ = 36.965903 | |

**Table 22**

**Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs**

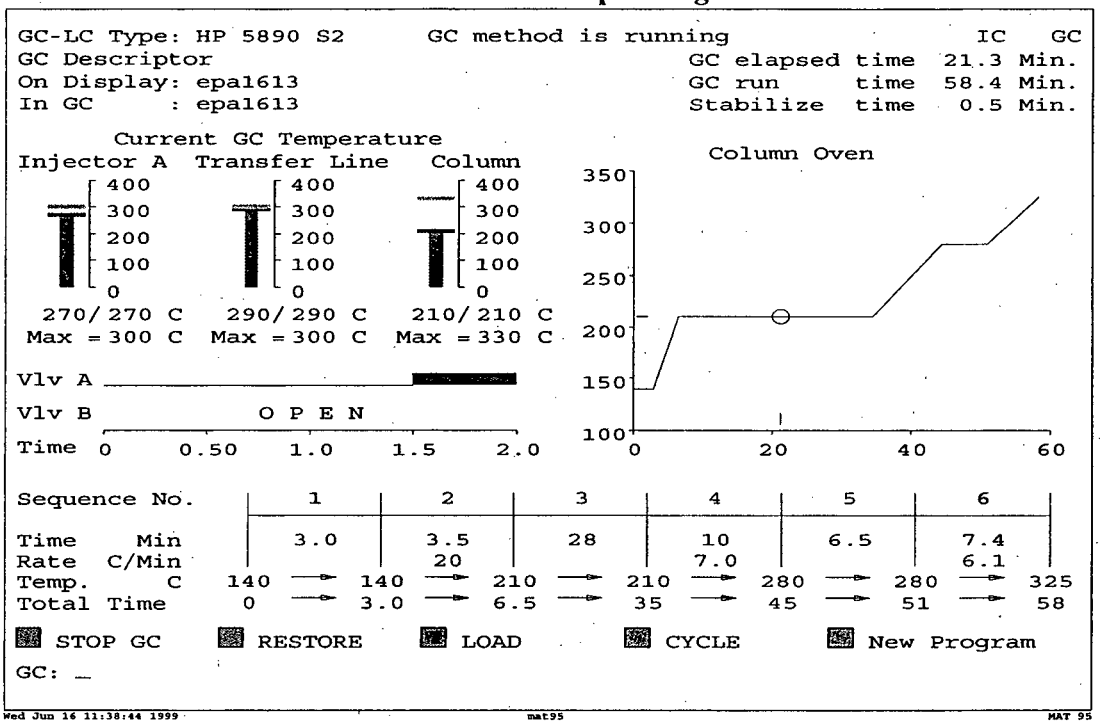
| Number of Chlorine Atoms | Ion Type | Theoretical Ratio | Control Limits Lower | Control Limits Upper |
|---|---|---|---|---|
| 4 | M/M+2 | 0.77 | 0.65 | 0.89 |
| 5 | M+2/M+4 | 1.55 | 1.32 | 1.78 |
| 6 | M+2/M+4 | 1.24 | 1.05 | 1.43 |
| 6[1] | M/M+2 | 0.51 | 0.43 | 0.59 |
| 7 | M+2/M+4 | 1.04/1.05[3] | 0.88 | 1.20 |
| 7[2] | M/M+2 | 0.44 | 0.37 | 0.51 |
| 8 | M+2/M+4 | 0.89 | 0.76 | 1.02 |

**Notes:**

1 Used for $^{13}$C-HxCDF (IS).
2 Used for $^{13}$C-HpCDF (IS).
3 Method 1613B Theoretical Ratio

## Figure 1

### Rtx-5 Recommended GC Operating Conditions




### DB-225 Recommended GC Operating Conditions

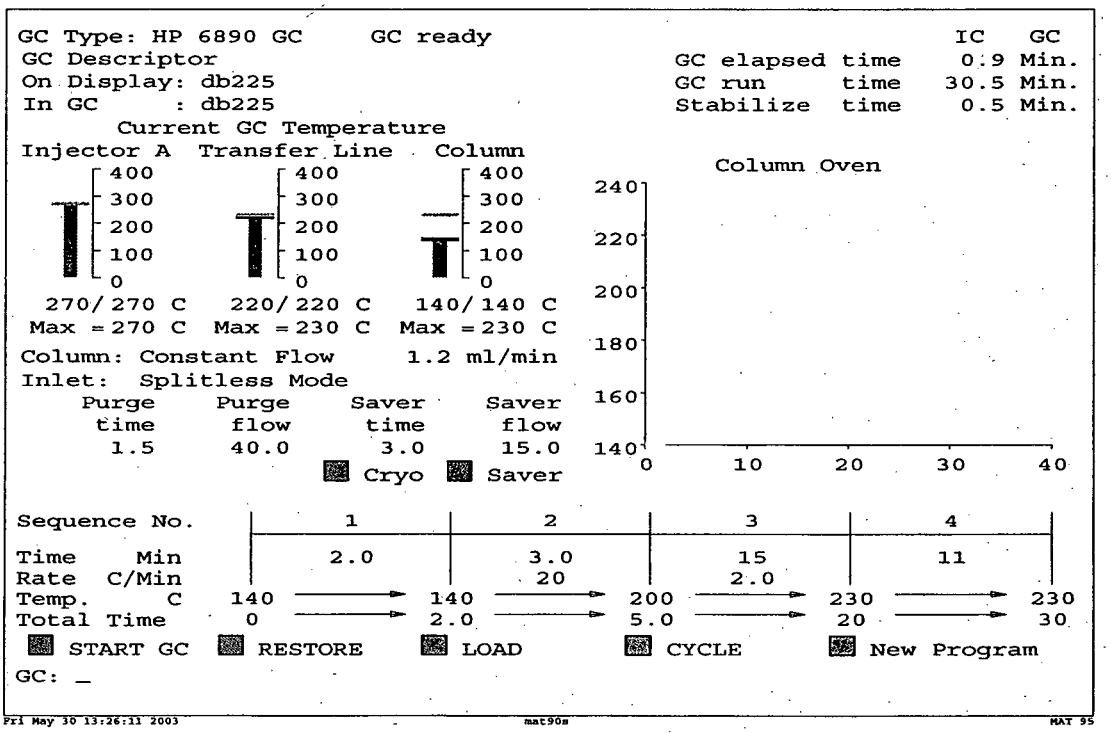
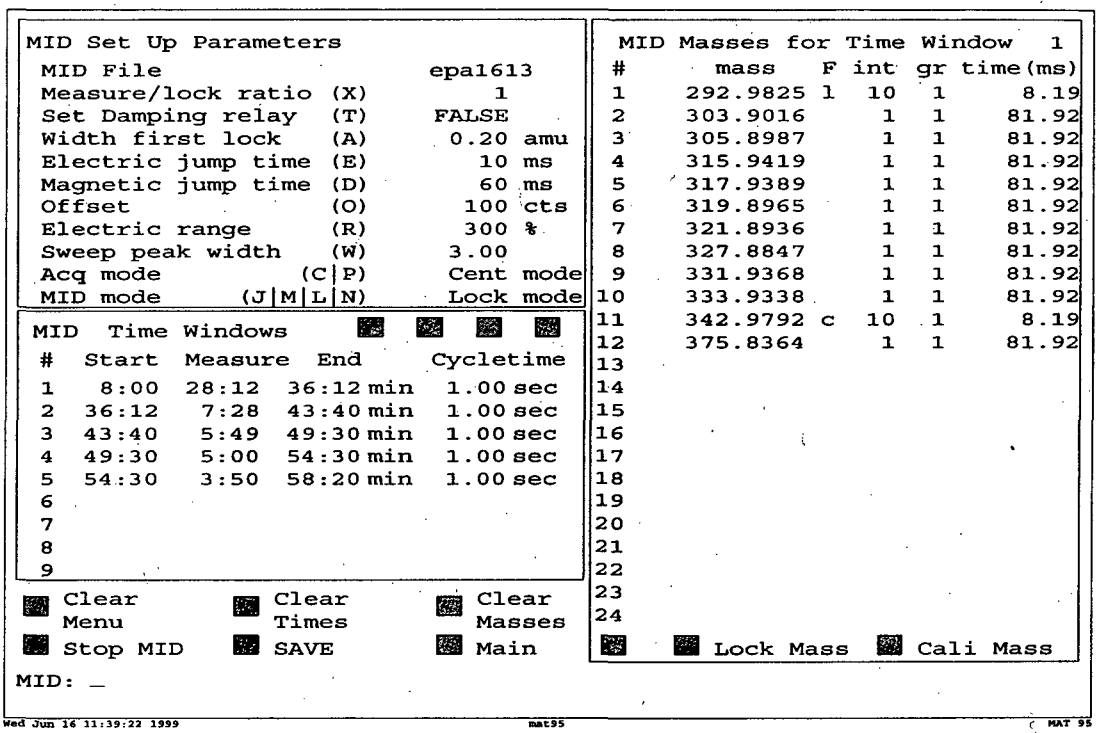


Figure 2

**Rtx-5 Recommended MID Descriptors**



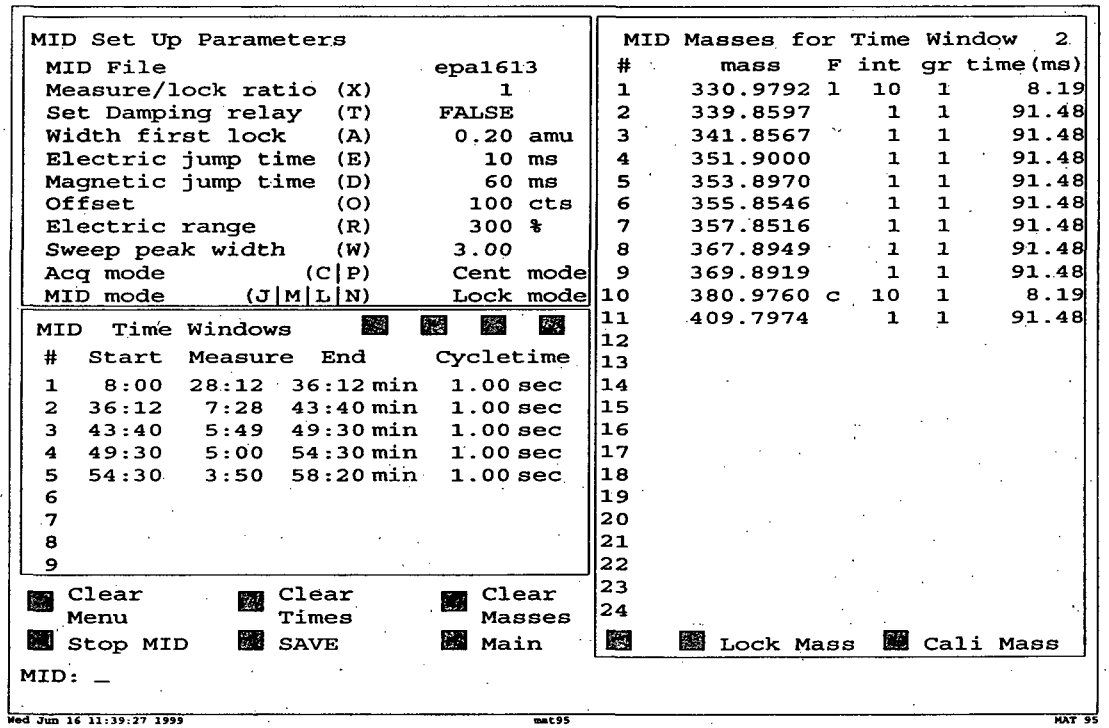



Figure 2 **Continued**

**Rtx-5 Recommended MID Descriptors**

```
MID Set Up Parameters
 MID File                          epa1613
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)           0.20 amu
 Electric jump time  (E)             10 ms
 Magnetic jump time  (D)             60 ms
 Offset              (O)            100 cts
 Electric range      (R)            300 %
 Sweep peak width    (W)           3.00
 Acq mode          (C|P)           Cent mode
 MID mode      (J|M|L|N)           Lock mode

MID  Time Windows
 #  Start  Measure  End       Cycletime
 1   8:00  28:12  36:12 min   1.00 sec
 2  36:12   7:28  43:40 min   1.00 sec
 3  43:40   5:49  49:30 min   1.00 sec
 4  49:30   5:00  54:30 min   1.00 sec
 5  54:30   3:50  58:20 min   1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Stop MID        SAVE            Main

MID: _
```

```
MID Masses for Time Window   3
 #      mass     F int  gr time(ms)
 1   373.8208       1   1    91.48
 2   375.8178       1   1    91.48
 3   380.9760 l    10   1     8.19
 4   383.8639       1   1    91.48
 5   385.8610       1   1    91.48
 6   389.8156       1   1    91.48
 7   391.8127       1   1    91.48
 8   401.8559       1   1    91.48
 9   403.8529       1   1    91.48
10   404.9760 c    10   1     8.19
11   445.7555       1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24
   Lock Mass   Cali Mass
```

Wed Jun 16 11:39:32 1999 mat95 MAT 95

```
MID Set Up Parameters
 MID File                          epa1613
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)           0.20 amu
 Electric jump time  (E)             10 ms
 Magnetic jump time  (D)             60 ms
 Offset              (O)            100 cts
 Electric range      (R)            300 %
 Sweep peak width    (W)           3.00
 Acq mode          (C|P)           Cent mode
 MID mode      (J|M|L|N)           Lock mode

MID  Time Windows
 #  Start  Measure  End       Cycletime
 1   8:00  28:12  36:12 min   1.00 sec
 2  36:12   7:28  43:40 min   1.00 sec
 3  43:40   5:49  49:30 min   1.00 sec
 4  49:30   5:00  54:30 min   1.00 sec
 5  54:30   3:50  58:20 min   1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Stop MID        SAVE            Main

MID: _
```

```
MID Masses for Time Window   4
 #      mass     F int  gr time(ms)
 1   404.9760 l    10   1     8.19
 2   407.7818       1   1    91.48
 3   409.7788       1   1    91.48
 4   417.8250       1   1    91.48
 5   419.8220       1   1    91.48
 6   423.7767       1   1    91.48
 7   425.7737       1   1    91.48
 8   435.8169       1   1    91.48
 9   437.8140       1   1    91.48
10   442.9728 c    10   1     8.19
11   479.7165       1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24
   Lock Mass   Cali Mass
```

Wed Jun 16 11:39:37 1999 mat95 MAT 95

## Figure 2 Continued

### Rtx-5 Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                          epa1613
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)           0.20 amu
 Electric jump time  (E)             10 ms
 Magnetic jump time  (D)             60 ms
 Offset              (O)            100 cts
 Electric range      (R)            300 %
 Sweep peak width    (W)           3.00
 Acq mode          (C|P)           Cent mode
 MID mode      (J|M|L|N)           Lock mode

MID  Time Windows
 #   Start  Measure  End        Cycletime
 1    8:00  28:12   36:12 min   1.00 sec
 2   36:12   7:28   43:40 min   1.00 sec
 3   43:40   5:49   49:30 min   1.00 sec
 4   49:30   5:00   54:30 min   1.00 sec
 5   54:30   3:50   58:20 min   1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Stop MID        SAVE            Main

MID: _
```

```
MID Masses for Time Window   5
 #      mass     F  int  gr  time(ms)
 1   430.9728    1   10   1     10.92
 2   441.7428        1   1    120.15
 3   443.7399        1   1    120.15
 4   457.7377        1   1    120.15
 5   459.7348        1   1    120.15
 6   469.7780        1   1    120.15
 7   471.7750        1   1    120.15
 8   480.9696    c   10   1     10.92
 9   513.6775        1   1    120.15
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

Wed Jun 16 11:39:43 1999 mat95 MAT 95

### DB-225 Recommended MID Descriptor

```
MID Set Up Parameters
 MID File                          db225
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          TRUE
 Width first lock    (A)           0.20 amu
 Electric jump time  (E)             10 ms
 Magnetic jump time  (D)             60 ms
 Offset              (O)            100 cts
 Electric range      (R)            300 %
 Sweep peak width    (W)           3.00
 Acq mode          (C|P)           Cent mode
 MID mode      (J|M|L|N)           Lock mode

MID  Time Windows
 #   Start  Measure  End        Cycletime
 1    8:00  22:30   30:30 min   1.00 sec
 2
 3
 4
 5
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Start MID       RESTORE         Main

MID: _
```

```
MID Masses for Time Window   1
 #      mass     F  int  gr  time(ms)
 1   292.9825    1   10   1      8.19
 2   303.9016        1   1     81.92
 3   305.8987        1   1     81.92
 4   315.9419        1   1     81.92
 5   317.9389        1   1     81.92
 6   319.8965        1   1     81.92
 7   321.8936        1   1     81.92
 8   327.8847        1   1     81.92
 9   331.9368        1   1     81.92
10   333.9338        1   1     81.92
11   342.9792    c   10   1      8.19
12   375.8364        1   1     81.92
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

Fri May 30 13:22:09 2003 mat90m MAT 95

**Figure 3**

**Example Sample Prep Benchsheets**

***STL Knoxville***

***Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group***

**QC Batch #:** **1296110** Method: Q8 DX1668_L

| Lot Number | Workorder | |
|---|---|---|
| H1J230000 | EMKL21AA | B |
| | EMKL21AC | C |
| | EMKL21AD | L |
| H1J100175 | ELWNN1AA | |
| | ELWNK1AA | |
| | ELWNQ1AA | |
| H1J100182 | ELWQR1AA | |
| | ELWQ01AA | |
| | ELWQ11AA | |
| | ELWQ41AA | |

Cleanup Standard Required (Methods F8, L1, Q8) ?:YES -- Add Method Required Cleanup Std

04-Dec-01 6:50:10 PM

Page 1 of 1

**Figure 3 Continued**

**Example Sample Prep Benchsheets**

***STL Knoxville***

***Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group***

**QC Batch No** 1296110 Relinquished to GC/MS By: _____ Date: _____

Received in GC/MS By: _____ Date: _____

| Work Order Numbe | | Column: DB-5 or RTX-5 | | | | Column: SPB-Octyl | | | | Column: DB-225 or RTX-225 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Date | Instrument | Analyst | Code | Date | Instrument | Analyst | Code | Date | Instrument | Analyst | Code |
| EMKL21AA | B | | | | | | | | | | | | |
| EMKL21AC | C | | | | | | | | | | | | |
| EMKL21AD | L | | | | | | | | | | | | |
| ELWNN1AA | | | | | | | | | | | | | |
| ELWNK1AA | | | | | | | | | | | | | |
| ELWNQ1AA | | | | | | | | | | | | | |
| ELWQR1AA | | | | | | | | | | | | | |
| ELWQ01AA | | | | | | | | | | | | | |
| ELWQ11AA | | | | | | | | | | | | | |
| ELWQ41AA | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |

**Comments:** _____

ID0005R1 04/04/01

**Figure 3 Continued**

**Example Sample Prep Benchsheets**

***STL Knoxville***

***Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group***

**QC Batch No:** 1296110 **Cleanup Std. Spiked By:** _____ **Verified By:** _____

| Work Order Number | | Cleanup Spike (Book:Page) | Cleanup Spike Volume (uL) | SilicaGel Alumina Col (Initial/Date) | Acid/Base Wash (Initial/Date) | Carbon Column (Initial/Date) | Florisil Column (Initial/Date) | Mercury Cleanup (Initial/Date) | TBA Cleanup (Initial/Date) | Other Cleanup (Initial/Date) | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|
| EMKL21AA | B | | | | | | | | | | |
| EMKL21AC | C | | | | | | | | | | |
| EMKL21AD | L | | | | | | | | | | |
| ELWNN1AA | | | | | | | | | | | |
| ELWNK1AA | | | | | | | | | | | |
| ELWNQ1AA | | | | | | | | | | | |
| ELWQR1AA | | | | | | | | | | | |
| ELWQ01AA | | | | | | | | | | | |
| ELWQ11AA | | | | | | | | | | | |
| ELWQ41AA | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |

**Comments:** _____

ID0053R1 4/6/05

**Figure 3 Continued**

**Example Sample Prep Benchsheets**

*STL Knoxville*

*Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group*

QC Batch No: 1296110 Internal Std. Spiked By: _____ Verified By: _____

| Work Order Number | | Filtered Y/N? | Vol of Sampling Surrogate (uL) | Soxhlet Started (Date/Time) | Soxhlet Finished (Date/Time | Blow Down (Initial/Date) | Recovery Standard (Book:Page) | Recovery Std Vol (uL) | Vol Delivered (uL) | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| EMKL21AA | B | | | | | | | | | |
| EMKL21AC | C | | | | | | | | | |
| EMKL21AD | L | | | | | | | | | |
| ELWNN1AA | | | | | | | | | | |
| ELWNK1AA | | | | | | | | | | |
| ELWNQ1AA | | | | | | | | | | |
| ELWQR1AA | | | | | | | | | | |
| ELWQ01AA | | | | | | | | | | |
| ELWQ11AA | | | | | | | | | | |
| ELWQ41AA | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |

**Comments:** _____

_____

_____

_____ W.B. Temp _____

Volume of Alt Standard: _____

Split Ratios: Post I.S. _____

Post F.C. _____

Post C.S. _____

Post R.S. _____

ID003-P1 04/04/01

# Figure 4

## Example Data Review Checklist

**STL Knoxville** **Specialty Organics Prep Batch Review/Checklist** **Batch #**_____

□ KNOX-ID-0004, rev. 6 (PCDD/F extraction) □ KNOX-ID-0012, rev. 1 (Air Train extraction) □ KNOX-ID-0013, rev. 4 (PCB extraction) □ KNOX-ID-0016, rev. 3 (LR-SIM PAH extraction) □ KNOX-ID-0017, rev. 1 (filters & XAD)

| *Review Items* | N/A | Yes | No | If No, why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Does the batch contain no more than 20 field samples? (Excluding MB, LCS, LCSD, MS, & MSD) | | | | | |
| 2. Were the samples extracted by the proper method? | | | | | |
| 3. Were the samples extracted within the required holding times? | | | | | |
| 4. For waters by 1613B, if visible solids were present, were solids determined to be ≤ 1%? | | | | | |
| 5. Were all project specific requirements met as noted on the Lot Checklists and Sample Worksheets? | | | | | |
| 6. Were all required QC samples prepared & extracted with the batch at method required frequency? | | | | | |
| 7. Were MS Run# properly assigned and samples entered on QC tracking Sheet? | | | | | |
| 8. Were samples requested properly and request form completed, signed, and dated? | | | | | |
| 9. Were the correct weights and volumes entered in Quantims for all samples? | | | | | |
| 10. Were the internal standards properly spiked and the spikes verified? Were the spike solution ID and spike volumes entered correctly and verified? | | | | | |
| 11. Were alternate standards properly spiked and the spikes verified? Were the spike solution ID and spike volumes entered correctly and verified? | | | | | |
| 12. Were all cleanup steps properly documented by initials and date? | | | | | |
| 13. Was the final volume checked and verified against the supplemental benchsheet and Quantims? | | | | | |
| 14. Are the final extracts free of water, precipitates, multiple phases, and color? | | | | | |
| 15. Were all appropriate notes and observations recorded on the prep benchsheet and in Quantims? | | | | | |
| 16. Were all Quantims batch information completed including;<br>• Batch reviewed<br>• Correct volumes entered<br>• Correct completion date entered<br>• Samples released | | | | | |
| 17. Does the prep batch paperwork package contain all required documentation which has been properly and completely filled out, including;<br>• Prep Benchsheet<br>• Supplemental Benchsheet<br>• Standard concentration forms or copies of logbook pages, for all IS, RS, SS, CS, Native and Alternate standards.<br>• Lot Checklists for all lots in the batch<br>• Sample worksheets for all samples in the batch in proper order as recorded on tracking sheet | | | | | |
| 18. Are all nonconformances documented appropriately and copy included with deliverable? | | | | | |

| **Analyst:** | **Date:** | **2nd Level Reviewer :** | **Date:** |
|---|---|---|---|
| **Comments:** | | **Comments:** | |
| | | | |
| | | | |
| | | | |

# Figure 4 Continued

# Example Data Review Checklist

**STL Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist**
**Method: 8290 - KNOX-ID-0004-R6**

| PFK Date/Time: | | Inst: | | Win Filename: | | Col Perf Filename: | |
|---|---|---|---|---|---|---|---|

| CS1 Filename | CS2 Filename | CS3 Filename | CS4 Filename | CS5 Filename |
|---|---|---|---|---|
| | | | | |

| *Review Items* | N/A | Yes | No | If No, why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Was the mass resolution documented before beginning the initial calibration? | | | | | |
| 2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)? | | | | | |
| 3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage? | | | | | |
| 4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group? | | | | | |
| 5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer? | | | | | |
| 6. Were the five calibration standard solutions, at the concentrations specified in Table 5 of the SOP, analyzed? | | | | | |
| 7. Was date/time of analysis verified between analysis header and logbook as correct? | | | | | |
| 8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 5), quantitation ions (Table 22), and formula (Section 10.2.6)? | | | | | |
| 9. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3? | | | | | |
| 10. Are %RSD ≤20% for all unlabeled native analytes? | | | | | |
| 11. Are %RSD ≤35% for all labeled internal standards? | | | | | |
| 12. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards? | | | | | |
| 13. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP? | | | | | |
| 14. Was the second source (Wellington) ICV standard analyzed, and the %D calculated and within the acceptance criteria of < ±35%? | | | | | |
| 15. If manual integrations were performed, are they clearly identified, initialed and dated? | | | | | |
| 16. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder? | | | | | |
| 17. Does the ICAL folder contain complete data in the following order? Data review checklist, a complete runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard, ICV Summary Table, Calculation Summary, and chromatograms? | | | | | |

| Analyst: | Date: | 2nd Level Reviewer : | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

# Figure 4 Continued

## Example Data Review Checklist

**STL Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist**
**Method: 8290 - KNOX-ID-0004-R6**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Start PFK: | | VER Filename: | | Win Filename: | | Inst: | |
| End PFK: | | VER Filename: | | Col Perf Filename: | | ICAL Date: | |

| *Review Items* | N/A | Yes | No | If No, why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Was the mass resolution documented at both the beginning and end of the 12 hour shift? | | | | | |
| 2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)? | | | | | |
| 3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage? | | | | | |
| 4. Was date/time of analysis verified between analysis header and logbook as correct? | | | | | |
| 5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group? | | | | | |
| 6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer? | | | | | |
| 7. Were continuing calibrations performed at the beginning and end of the 12-hour period, with successful mass resolution and GC resolution performance checks? | | | | | |
| 8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 3), quantitation ions (Table 22), and formula (Section 10.2.6)? | | | | | |
| 9. Are the measured RRFs for each compound within the specified control limits in Table 7 for all PCDDs/PCDFs? | | | | | |
| 10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3? | | | | | |
| 11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards? | | | | | |
| 12. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP? | | | | | |
| 13. If manual integrations were performed, are they clearly identified, initialed and dated? | | | | | |
| 14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder? | | | | | |
| 15. Does the CCAL folder contain complete data in the following order: Data review checklist, a complete runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards? | | | | | |
| | | | | | |

| Analyst: | Date: | 2nd Level Reviewer : | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

# Figure 4 Continued

## Example Data Review Checklist

**STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist** **LOT #**_____
**Method: 8290 - KNOX-ID-0004-R6** **Page 1 of 2**

**Batch Number:**

| *Review Items* A. Initial Calibration | N/A | Yes | No | Why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.) | | | | | |
| **B. Continuing Calibration** | | | | | |
| 1. Has a Continuing Calibration Checklist been completed for each analytical batch? | | | | | |
| **C. Client Sample AND QC Sample Results** | | | | | |
| 1. Were all special project requirements met? | | | | | |
| 2. Were the header information, prep factors, and dilution factors verified? | | | | | |
| 3. Was date/time of analysis verified between analysis header and logbook as correct? | | | | | |
| 4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____ | | | | ☐ HT expired upon receipt.<br>☐* Client requested analysis after HT expired.<br>☐ Re-extraction done after HT expired.<br>☐ See Comment no. | |
| 5. Are internal standards within QC limits specified in Table 13? *If no, list samples and reason (e.g., surl):* Sample / Reason / Sample / Reason | | | | ☐* **[sup]** Ion suppression due to matrix.<br>☐* **[low]** Low recovery. S/N >10 and EDL<ML.<br>☐ **[sam]** Not enough sample to re-extract.<br>☐ **[dil]** Dilution showed acceptable %R.<br>☐ **[mtx]** Obvious matrix interference. Further cleanup not possible.<br>☐* **[unk]** At client's request, data was flagged as estimated and released without further investigation.<br>☐ **[com]** See Comment no. _____. | |
| 6. Were the following qualitative criteria met for all reported PCDD/Fs:<br>• All 2378 isomers within the RRT limits specified in Table 3 and both ions maximized within ±2 seconds.<br>• All non-2378 isomers within established RT windows and both ions maximized within ±2 seconds.<br>• The ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22.<br>• All peaks ≥2.5 S/N.<br>• No corresponding peak at PCDPE mass. | | | | | |
| 7. Were peaks ≥2.5 S/N, which did not meet the above criteria, properly calculated and reported as EMPCs? | | | | | |
| 8. Were all positive 2378-TCDF hits confirmed by analysis on DB-225? | | | | | |
| 9. Are positive results within calibration range? *If no, list samples:* _____ | | | | ☐ OCDD/F or non-2378 exceeded calibration range<br>☐ Sample extracted at lowest possible volume | |
| 11. If manual integrations were performed, are they clearly identified, initialed and dated? | | | | | |
| 12. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.) | | | | | |
| 13. Was a narrative prepared and all deviations noted? | | | | | |

* Such action must be taken in consultation with client.

# Figure 4 Continued

## Example Data Review Checklist

**STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist** **LOT #**_____
**Method: 8290 - KNOX-ID-0004-R6** **Page 2 of 2**

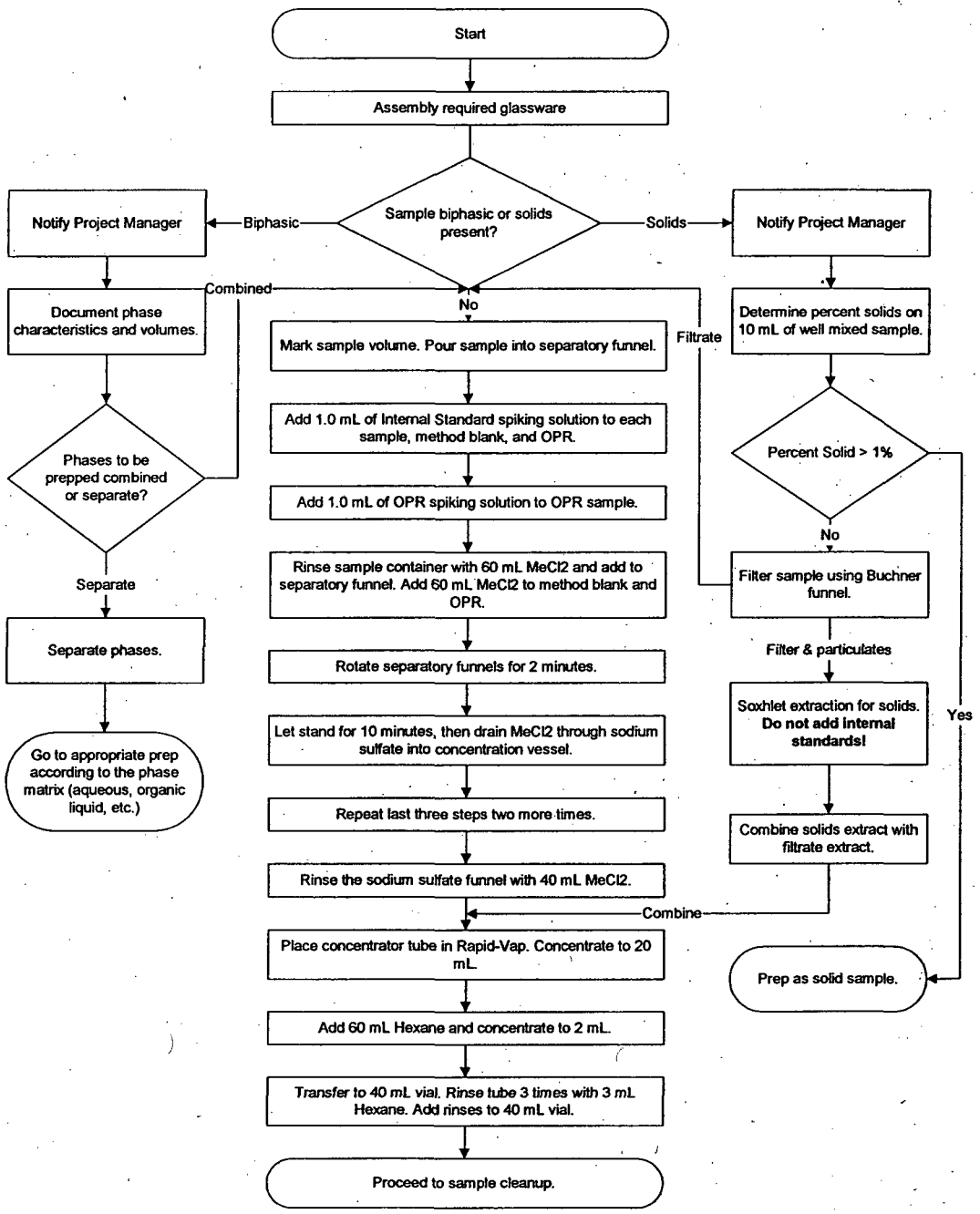
| D. Preparation/Matrix QC | N/A | Yes | No | Why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. LCS(OPR) done per prep batch and all analytes within the limits specified in QuantIMS reference data? *If no, list LCS(OPR) ID:* _____ | | | | ☐* Reanalysis not possible-insufficient sample.<br>☐ LCS %R high and affected analyte(s) were <ML in associated samples.<br>☐ See Comment no. _____. | |
| 2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence? | | | | | |
| 3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____ | | | | ☐* Internal standards are high and blank demonstrates that analysis is free of contaminants.<br>☐* Sample internal standards OK and there is no analytes >ML in samples associated with blank. | |
| 4. Are all analytes present in the method blank ≤ ML? *If no, list blank ID:* _____ _____ _____ | | | | ☐ Sample results are > 20x higher than blank.<br>☐*. There is no analyte > RL in the samples associated with method blank.<br>☐* Reanalysis not possible-insufficient sample | |
| 4. MS/MSD done per batch and are all recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD ID:* _____ _____ _____ _____ _____ | | | | ☐ LCS showed acceptable results indicating sample matrix effects.<br>☐ LCS showed acceptable results. High native analyte concentration relative to spike level.<br>☐ LCS showed acceptable results. RPD out due to lack of sample homogeneity.<br>☐ See Comment no. _____. | |
| E. Other | | | | | |
| 1. Are all nonconformances documented appropriately and copy included with deliverable? | | | | | |

| Analyst: | Date: | Analyst: | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

* Such action must be taken in consultation with client.

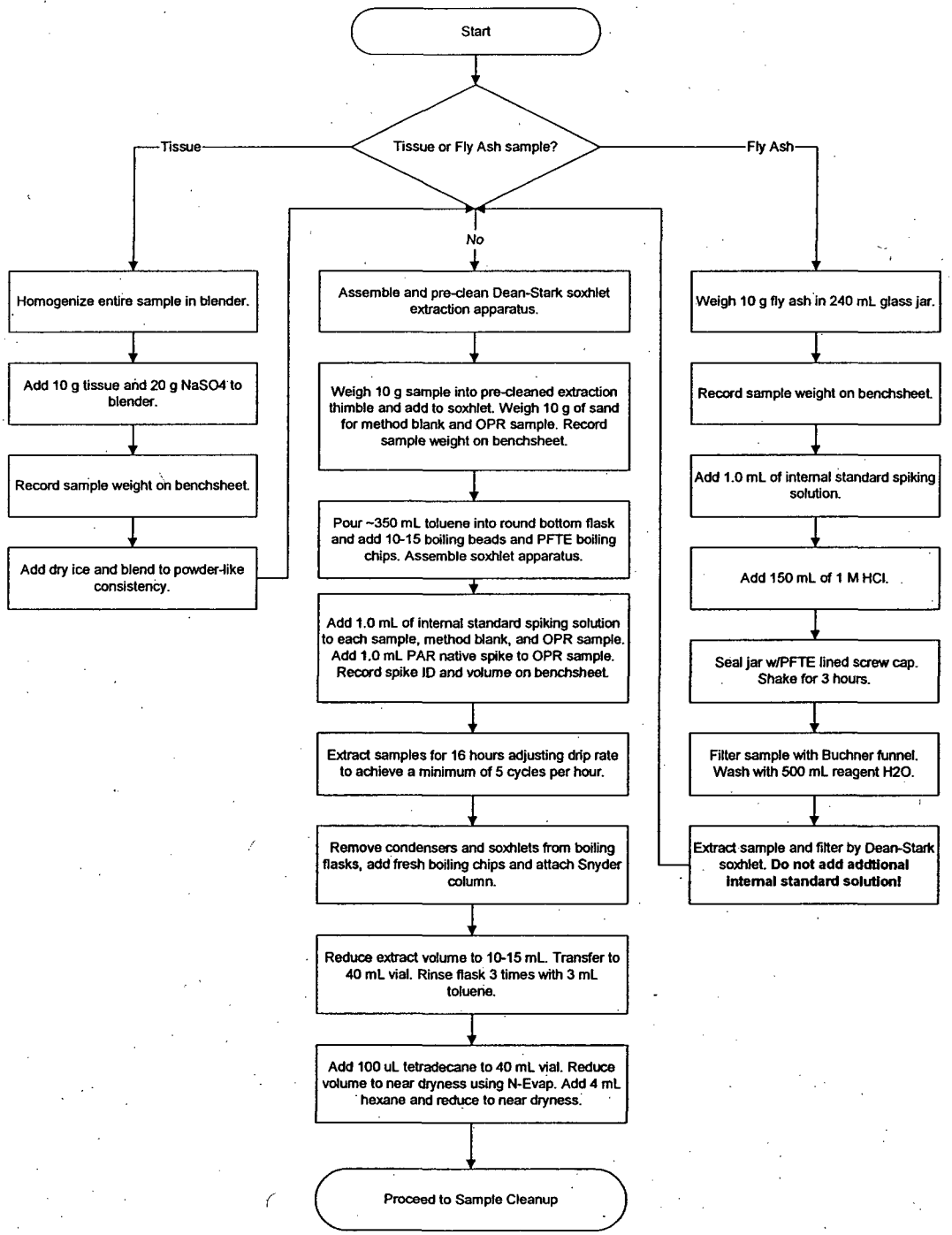
# Figure 5

## Aqueous Sample Extraction Flowchart



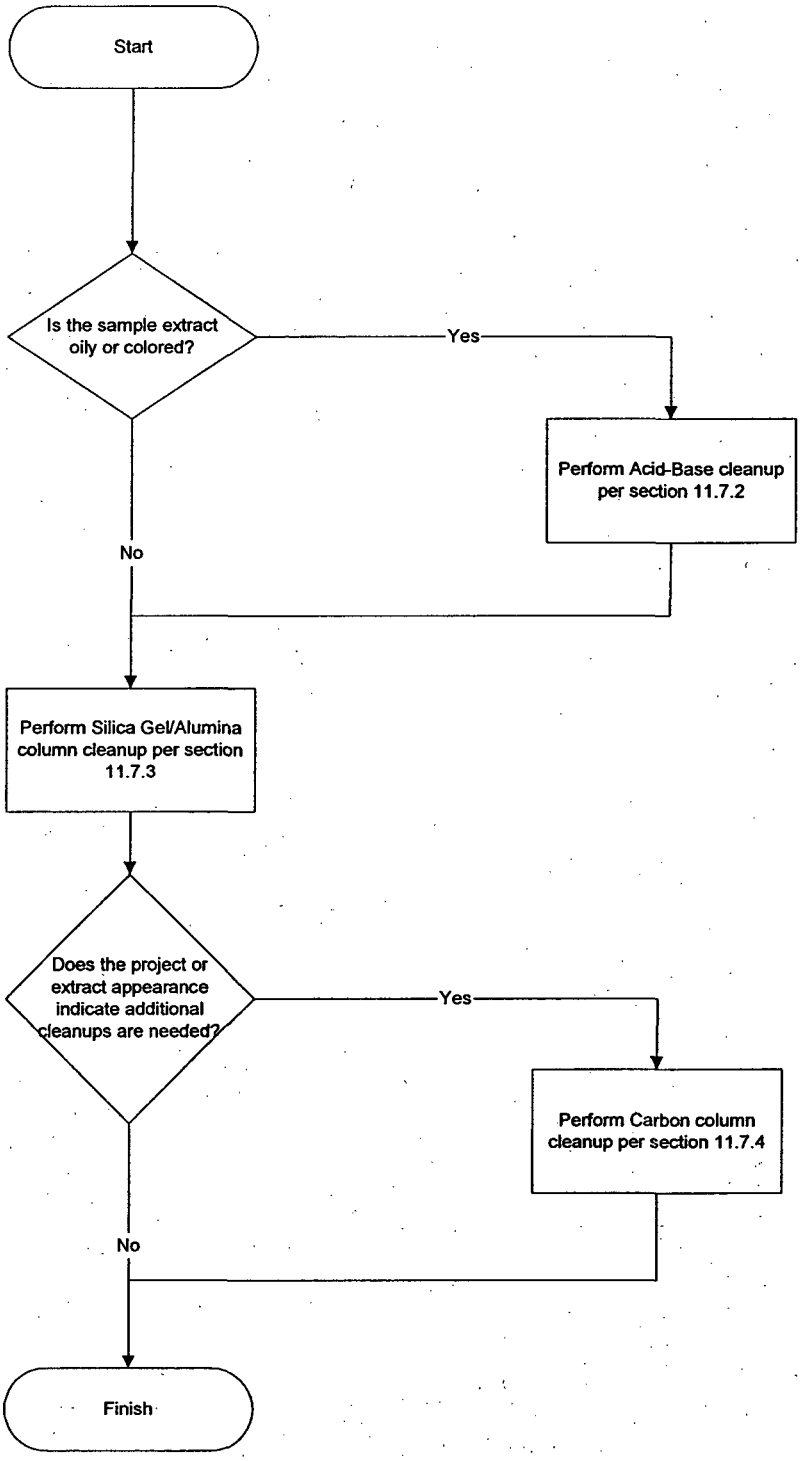
## Figure 6

## Solid Sample Extraction Flowchart



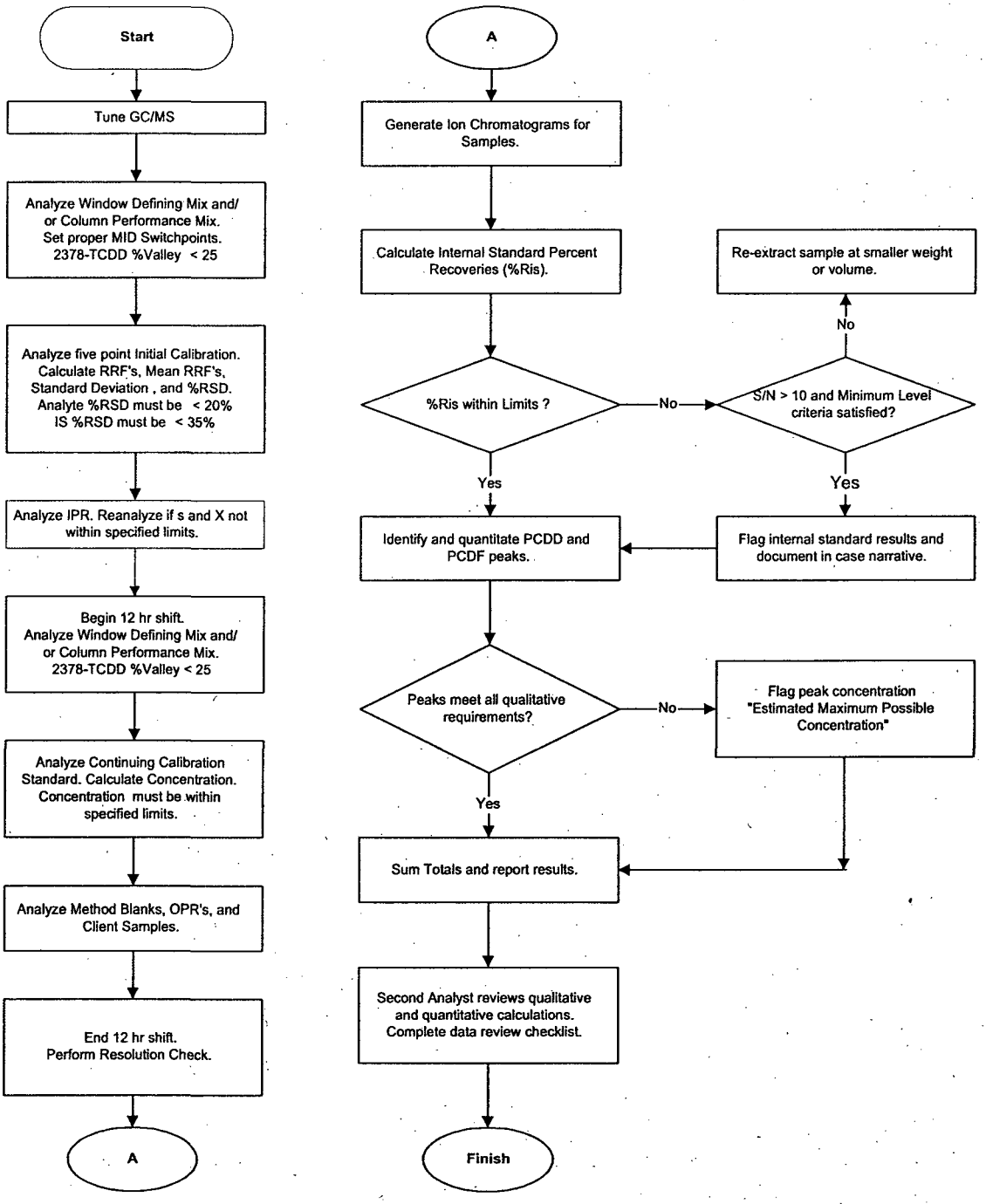
## Figure 7

## Sample Cleanup Flowchart



## Figure 8

## Analysis Of PCDD's and PCDF's by HRGC/HRMS



## Appendix I

## Evaluation of Method Blank Criteria for USACE Programs

### 18. Scope and Application

18.1 This modification to the standard procedure is designed to meet analytical program requirements for USACE Hazardous, Toxic and Radioactive Waste (HTRW) Projects. This procedure is based on the document entitled "Shell for Analytical Chemistry", US Army Corps of Engineers (USACE), EM200-1-3, Appendix I, 1 Feb 01.

18.2 This procedure modifies the evaluation and acceptance criteria for Method Blanks.

18.3 This procedures establishes Method Quantitation Levels (MQLs) based on Minimum Levels (MLs) and extract volumes that are specified in USEPA Method 8290.

### 19. Summary of Method

19.1 Same as the base procedure with the following exception.

19.2 Method blanks are evaluated based on the criteria specified in section 11.4.1 of the USACE "Shell".

### 20. Definitions

20.1 MDL Check Sample Concentration - The MDL Check sample concentration is one half of the Method Quantitation Level (MQL).

20.2 MQL - Method Quantitation Level - The MQL represents the value that the laboratory has demonstrated the ability to reliably quantitate target analytes. The MQLs for this method have been established based on the reference method calibration levels, required initial sample extraction weight/volume, and the recommended final extract volume.

20.3 Common Laboratory Contaminant - A target analyte which is present in the method blank due to environmental levels or reagent contamination which is beyond the control of the laboratory. For the purposes of this method, Octachlorodibenzodioxin is has been determined to be a common laboratory contaminant.

### 21. Procedure

21.1 The acceptance criteria in section 9.3 are replaced with the following;

The following criteria shall be used to evaluate the acceptability of the method blank data if project DQOs do not specify otherwise: The concentration of all target analytes shall be below the MDL check sample concentration for each target analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample results for the same analyte, whichever is greater for the MB to be acceptable. When this criterion is exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the

method blank. However, sample corrective action may be limited to qualification for blank contamination (i.e., B-flag). When the concentration of any target analytes within the MB are above the MDL check sample for the majority of the target analytes or above the MQL for target analytes known to be common laboratory contaminants, assess the effect this may have on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source of this contamination in the method blank. The case narrative should discuss this situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank, and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method blank and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.

## 22. References

22.1 US Army Corps of Engineers (USACE), EM200-1-3, Appendix I, 1 Feb 01, Shell for Analytical Chemistry Requirements.

**Table 23**

**Method Quantitation Levels[1] for USACE NTRW Projects**

| Native Analyte | Water (pg/L) | Solid (pg/g) | Tissue (pg/g) | Wipe (pg) | Air (pg) | Waste (pg/g) |
|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 20 | 2.0 | 2.0 | 20 | 20 | 20 |
| Total TCDD | 20 | 2.0 | 2.0 | 20 | 20 | 20 |
| 2,3,7,8-TCDF | 20 | 2.0 | 2.0 | 20 | 20 | 20 |
| Total TCDF | 20 | 2.0 | 2.0 | 20 | 20 | 20 |
| 1,2,3,7,8-PeCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| Total PeCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,7,8-PeCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 2,3,4,7,8-PeCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| Total PeCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,4,7,8-HxCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,6,7,8-HxCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,7,8,9-HxCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| Total HxCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,4,7,8-HxCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,6,7,8-HxCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 2,3,4,6,7,8-HxCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,7,8,9-HxCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| Total HxCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,4,6,7,8-HpCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| Total HpCDD | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,4,6,7,8-HpCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| 1,2,3,4,7,8,9-HpCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| Total HpCDF | 50 | 5.0 | 5.0 | 50 | 50 | 50 |
| OCDD | 100 | 10. | 10. | 100 | 100 | 100 |
| OCDF | 100 | 10. | 10. | 100 | 100 | 100 |

(1) MQLs are based on the method calibration limits specified in Table 1 of USEPA Method 8290 assuming a 20µL final extract volume as specified in section 7.8.1 of that method.

| STL Edison Standard Operating Procedure | Revision Date: 04/06/04 |
|---|---|
| Title: SW8082 - Analysis of Polychlorinated Biphenyls by Gas Chromatography | |
| Laboratory Director: _____ | SOP Number 808204 |
| Technical Director: _____ | |
| QA Manager: _____ | REV 4 |
| Department Manager: catalina R. Belanger | Page 1 of 23 |
| File Location: F:\QAQC\SOPs\NELAC\NELAC SOPs 2004\120PEPCB\SW846\808204.DOC | |

UNCONTROLLED COPY

## 1. SCOPE AND APPLICATION

1.1. The general principles of Method 8082 can be applied to any gas chromatographic system. The procedure covers all aspects of normal daily activities for GC operation used for the analysis of the Polychlorinated Biphenyls (PCBs) listed in Table 1 in extracts of solid and liquid matrices, using fused silica, open tubular, capillary columns with electron capture detectors (ECD).

1.2. This procedure specifically addresses quantitative and confirmatory analysis of PCBs using Agilent Technologies brand equipment. The samples analyzed are primarily environmental samples of soil, waste, water and leachate. This method covers all aspects of analysis of PCBs except for those aspects that pertain to extraction and clean up.

**Table 1**
**Polychlorinated Biphenyls**

| Compound Name | CAS Registry No. |
|---|---|
| Aroclor 1016 | 12674-11-2 |
| Aroclor 1221 | 11104-28-2 |
| Aroclor 1232 | 11141-16-5 |
| Aroclor 1242 | 53469-21-9 |
| Aroclor 1248 | 12672-29-6 |
| Aroclor 1254 | 11097-69-1 |
| Aroclor 1260 | 11096-82-5 |
| Aroclor 1262 | 37324-23-5 |
| Aroclor 1268 | 11100-14-4 |

## 2. SUMMARY OF METHOD

2.1. A measured volume or weight of sample (15 g for soil, 1 g for waste, 1000 ml for water, and 100 ml for TCLP) is extracted using the appropriate matrix-specific sample extraction technique. The extract is exchanged to hexane and concentrated to a final volume between 5 and 20 ml.

2.2. Liquid samples are extracted at neutral pH with methylene chloride using either Method 3510C (separatory funnel) or Method 3520C (continuous liquid-liquid extractor)

2.3. Solid samples are extracted with hexane-acetone (1:1) using Method 3550B (ultrasonic extraction) or Method 3541 (automated soxhlet extraction). Both neat and diluted organic liquids (Method 3580A, Waste Dilution) may be analyzed by direct injection.

2.4. Extract cleanup steps are employed depending on the nature of the matrix interferences. Suggested cleanups include Florisil (Method 3620B), TBA for sulfur (Method 3660B), and Sulfuric Acid Permanganate for heavy organic interferences (Method 3665A).

2.5. After cleanup, the extract is analyzed by injecting a 2-uL sample into a Agilent Technologies gas chromatograph equipped with a dual wide-bore fused silica capillary columns and dual electron capture detectors (GC/ECD).

2.6. Samples are analyzed after all the necessary checks have been performed. An Aroclor calibration verification standard must be run prior to PCB analysis. Its failure would indicate the need for recalibration.

2.7. Acquired data from sample analysis is manually reviewed. Secondary column confirmation of target compounds and quantitation are conducted by the analyst as required.

3. DEFINITIONS:

3.1. Refer to document DEFDOC-04 for definitions.

4. INTERFERENCES

4.1. Interferences from phthalate esters introduced during sample preparation can pose major difficulties for PCB determinations.

4.1.1. Interferences from phthalate esters can be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

4.2. The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting PCBs. Sulfur contamination should be expected with sediment samples. Employ SW3660B for removal of sulfur.

4.3. Co-eluting chlorophenols are eliminated by using SW3620B (Florisil).

4.4. Interferences from other organic compounds can effectively be removed using acid permanganate treatment, Method 3665A. This destructive technique can be employed only when the sample extract is being analyzed solely for PCBs.

5. APPARATUS AND MATERIALS

5.1. Gas Chromatograph:

5.1.1. Agilent Technologies (Avondale, PA) model 6890 Gas Chromatograph (G.C.), equipped for simultaneous quantitation and confirmation columns using two separate detector channels on dual megabore capillary columns that are suitable for the analysis of organochlorine pesticides and PCB's. All operations are as automated as possible with the equipment utilized.

5.1.2. Injection system: Sample injection is accomplished by a single auto injector. The auto injector is serviced by a robot arm that shuttles a single sample between the sample tray and the injector turret.

5.1.2.1. The sample is injected into a split/splitless injection port equipped with electronic pressure control (EPC). The injection port is normally operated in splitless mode during injection. The EPC is operated in the constant pressure mode.

5.1.3. Liners: The injection port is each fitted with a replaceable, heavy-walled glass double gooseneck liner. The liner contains a plug of silanized glass wool approximately 1 cm in length. The glass wool is positioned in the liner between the double gooseneck. The liner is replaced on a regular maintenance schedule.

5.1.4. Oven and Columns: Temperature programmable gas chromatograph ovens are required, capable of integrated temperature control between 35°C and 350°C.

5.1.4.1. Two dissimilar columns are used for analysis. A Restek StxCLPesticides, 30m x 0.53mm ID x 0.5um film thickness column is used for sample quantitation. The secondary column is a Restek StxCLPesticides II, 30m x 0.53mm ID x 0.42um film thickness column.

5.1.5. Detectors: Sample detection is by electron capture. The G.C. is equipped with dual Electron Capture Detectors (ECD), one for each column.

5.1.5.1. Each detector is supplemented with make-up gas to provide sufficient detector flow for maintaining the electron plasma. This is in addition to the gas exiting the column. The make-up gas (P-5) is fed from a supply other than the injection port.

5.2. Data System:

5.2.1. The data system consists of Agilent Technologies GC Chemstation Revision A.08.02 and Agilent Technologies Enviroquant Chemstation G1701AA Version A.03.00 upgraded to A.03.02 which is used for acquisition and Target software (Thru-Put Systems) using a Falcon integrator for data processing.

6. REAGENTS

6.1. Gases: Ultra high purity (99.999%) Helium is used as the carrier and injection port purge gas. It is introduced to the GC at the injection port. Ultra high purity (99.999%) Argon (95%) / Methane (5%) (a.k.a. P-5 Mixture) is used as make-up gas. It is introduced to the GC via the make-up gas adapter at the end of the capillary column. They are supplied by M-G Industries (Valley Forge, PA). Both gases are supplied at tank pressures of 2000-2400 psig. for a 300 cft. tank. The tank pressure is regulated to an outlet pressure of 70 psig. Each tank is used until the tank pressure drops to less than 500 psig.

6.1.1. The gas streams are polished using three traps or filters before introduction to the G.C. The traps are as follows:

6.1.1.1. Hydrocarbon trap
6.1.1.2. $H_2O$ trap

6.1.1.3. $O_2$ scrubber

6.1.2. Both the moisture trap and the Oxygen scrubber are of the indicating type. They require either replacement or reconditioning upon color change of the active agents. Refer to the instructions for the individual traps to determine if it is still active. The hydrocarbon trap is a simple activated carbon trap. With high quality gas, it should last for an extended period of time (1-yr. minimum).

6.2. Solvents used in the extraction and clean up procedures include Hexane, Methylene Chloride, and Acetone that are exchanged to Hexane prior to analysis.

6.3. Hexane is required in this procedure. All solvents must be pesticide quality or equivalent. Each lot of solvent is screened for contaminants before being used for analysis.

7. STANDARDS

7.1. Standards are purchased as a concentrated solution. Standard compounds or mixtures for this analysis include an Aroclor 1016/1260 mix, Aroclor 1221, 1232, 1242,1248, 1254,1262, 1268 and the surrogate compound Decachlorobiphenyl (DCB).

NOTE: Two independent sources are used for quantitation standards and spiking standards

7.1.1. Most stock solutions are diluted (in volumetric glassware) to working concentration using hexane as the diluent.

7.2. Standard mixes and sources: *

| | |
| --- | --- |
| TCMX/DCB | Supelco – 48460 |
| TCMX/DCB Spike Mix | Supelco – 861275 |
| Ar1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 | Supelco – 48097, 48098, 44805, 44806, 44807, 44808, 44809, 44810, 502146 |
| Aroclor 1660 Spike Mix | Supelco – 861274 |

*Suppliers with equivalent standards are also used.

7.2.1. Solution Preparation

7.2.1.1. 2500 ppb solution (200ppb DCB/TCMX): 250ul of 0.1ug/ul, A1016/1260 stock, 100ul of .2ug/ul TCMX/DCB, Dilute to 100ml

7.2.1.2. 1500 ppb solution (150ppb DCB/TCMX): 150ul of 0.1ug/ul, A1016/1260 stock, 75ul of .2ug/ul TCMX/DCB, Dilute to 100ml

7.2.1.3. 1000 ppb solution (100ppb DCB/TCMX): 500ul of 1.0ug/ul A1016/1260 stock, 250ul of .2ug/ul TCMX/DCB, Dilute to 500ml

7.2.1.4. 500 ppb solution (50ppb DCB/TCMX): 50ul of 1.0ug/ul A1016/1260 stock, 25ul of .2ug/ul TCMX/DCB, Dilute to 100ml

7.2.1.5. 100 ppb solution (25ppb DCB/TCMX): 10ul of 1.0ug/ul A1016/1260 stock, 12.5ul of .2ug/ul TCMX/DCB, Dilute to 100ml

7.2.2. Surrogate Spiking Solution

7.2.2.1. 10ppm DCB & TCmX Mix Solution, custom blend in final volume of 50 ml (Acetone)

7.2.3. Surrogate Oil Spiking Solution

7.2.3.1. 0.5 ppm DCB & TCmX Oil Solution, 2.5 ml of 10 ug/ml solution, dilute to 50 ml (Acetone)

7.2.4. Aroclor 1016/1260 Spiking Solution

7.2.4.1. 100ppm A1016/1260 Mix Solution, custom blend in final volume of 10 ml (Acetone)

7.2.5. Aroclor 1016/1260 Oil Spiking Solution

7.2.5.1. 5.0 ppm A1016/1260 Mix Solution, 0.5 ml of 100 ug/ml solution, dilute to 10 ml (Acetone)

7.2.6. Individual Aroclor Sol'ns: 1221, 1232, 1242, 1248, 1254, 1262, 1268;

7.2.6.1. 1000 ppb solution (100ppb DCB/TCMX) 200ul of 1.0ug/ul Individual Aroclor solution, 100ul of 0.2 ug/ul TMX/DCB, dilute to 200ml

## 8. PRESERVATION AND HANDLING

8.1. Extracts must be stored under refrigeration in the dark and analyzed within 40 days of extraction.

8.2. Extract Cleanup:

8.2.1. Cleanup methods are dictated by the original sample matrix and the parameters being determined.

8.2.2. Cleanup of all water samples, if needed, is performed using Sulfuric Acid Permanganate and/or TBA sulfite. Blanks must also undergo cleanup following the same procedures as samples.

8.2.3. Cleanup of all soil samples is conducted using TBA sulfite and Sulfuric Acid Permanganate. Blanks must also undergo cleanup following the same procedures as samples.

8.2.4. Cleanup using Sulfuric Acid Permanganate effectively destroys the majority of organic material in the sample extract and should be used only when PCB is the only analysis to be performed on the sample extract.

## 9. SAFETY

9.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

9.2. The analyst must wear a protective lab coat, safety glasses, and gloves when handling all samples, extracts, standards and solvents.

9.3. All questions pertaining to any safety procedure should be brought to the department manager or STL Edison Safety Officer.

9.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

9.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Hexane | Flammable Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Methylene Chloride | Carcinogen Irritant | 25 ppm-TWA 125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

10. PROCEDURE

10.1. GAS CHROMATOGRAPH OPERATION

10.1.1. The sequence of events for G.C. analysis involves many steps that must be performed on each analytical column. First the injection system and column performance and calibration must be verified. Maintenance operations are performed as needed. Then samples must be run on the instrument. Chromatograms and reports must be evaluated for content, integration and concentration. Re-runs and dilutions must be made based on the calibrations that were in effect at the time the sample was run. A detailed review of acquired data files is conducted immediately prior to initiating the final calculations to determine the concentrations of target analytes.

10.1.2. Instrument Operating Parameters:

9.5.1.1. Injection System: A splitless injection port with electronic pressure control (EPC) is used. Seventy-five seconds after sample injection, the purge valve is turned on to facilitate the sweeping of any remaining residual solvent/sample from the injection port. The EPC is used in the pressure Ramp mode.

9.5.1.2. The EPC is used in the ramp pressure mode. The ramp pressure program is as follows:

| Initial Pressure | InitialTime | Rate | Final Pressure | Hold |
| --- | --- | --- | --- | --- |
| 25 psi | 0.50 min | 20psi/min | 20 psi | 2.00 min |
| | | 8 psi/min | 12 psi | 6.60 min |
| | | 10.0 min | 16 psi | 2.00 min |

10.1.2.1. For PCB analysis the normal operating conditions of the injection port are as follows:

| | |
| --- | --- |
| Injection Temperature: | 250°C |
| Injection Port Pressure: | 25ml/min |
| Column flow: | 33.2 ml/minute |
| Split vent flow: | 60.0 ml/minute |
| Purge vent flow: | 1.2 ml/minute |

EPC: Ramp Constant

10.1.2.2. In addition to the EPC, the injection port is also equipped with a glass double goose neck liner that contains a 1-cm glass wool plug. The plug of glass wool is located in the liner between the double goose neck.

10.1.2.3. This liner/glass wool combination provides many functions. The glass wool serves as a heat sink rapidly vaporizing solvent and samples resulting in higher response factors. The liner also protects the column head from accumulation of high boiling residuals and particulates.

10.1.2.4. Regular maintenance is performed on the injection port. When the glass wool/liner is changed, the septa also must be changed. Injection port, oven and detector temperatures are lowered to ambient prior to "cracking" the system. This is so as to introduce a minimum of damaging oxygen molecules into the system.

10.1.2.5. After the system has cooled, the old liner is removed. The injection port should be checked for particulate residues and cleaned as needed. A flashlight is usually required for this. After a new liner has been prepared it is placed into the injection port. A graphite seal is placed around the liner. The edges of the seal must be flat, not knife-edged, and free of nicks or burrs. If any of these conditions are not met, the graphite seal must be replaced as well. The graphite seal is critical to proper operation of the injection port. If in doubt, replace it.

10.1.2.6. The locking ring on the top of the injection port should be turned, with the wrench, about 1/8 turn past finger tight. The septum nut should never be tightened more than finger tight. After the injection port is reassembled, all column nuts inside the oven should be checked for leaks using Snoop (Supelco) or another suitable leak tester.

10.1.2.7. The septa should be changed each time the injection port is opened. Another routine maintenance operation to improve column performance is the removal of the first 3 cm of the column.

10.1.2.8. Once the signal from both detectors has stabilized, it is time to re-heat the zones. The zones should be heated in the order of detectors, oven and then injectors. This is to ensure that volatilized contaminants do not condense on the column or detector.

10.1.2.9. Oven: With the megabore columns installed, temperature programming is employed to achieve higher resolution of compounds and shorter run times than could be accomplished using isothermal methods.

10.1.2.9.1. The oven program and pressure ramping for PCB analysis is employed for all columns as follows:

| Initial Temp | Hold Time 1 | Rate1 | Temp1 |
|---|---|---|---|
| 164°C | 0.0min | 12°/min | 234°C |
| **Hold Time2** | **Rate2** | **FinalTemp** | **FinalTime** |
| 2.4 min | 40°/min | 325°C | 1.5min |

10.1.2.10. Detectors: Operate detectors at 330°C, supplement column flow with make-up gas for a combined total flow of 60 ml/min. They are essentially maintenance free on a day-to-day basis. They are routinely baked out at 350°C to remove persistent contaminants. On occasion the detectors may be baked out at a higher temperature to remove contaminants with an extremely high boiling point (CAUTION: Do not exceed the maximum detector temperature of 380°C).

10.1.2.10.1. If the detectors are particularly contaminated, they must be sent to Agilent Technologies in Avondale, Pennsylvania for reconditioning. This should occur if the detector baseline is greater

than 100 Hz. Detector reconditioning should be required at a maximum of biannually.

10.1.2.11. Chemstation: The Chemstation is responsible for automation of runs and acquisition. The system is dedicated to a single GC and does not multitask. Therefore, data manipulation cannot be done while sample analysis is in progress. The data system acquires and stores all chromatographic data.

10.1.2.12. Target: Target is responsible for the processing of the data files. Calibrations, verification standards and samples are processed and reviewed using this database. All reports are also generated by Target.

10.2. EXTERNAL STANDARD CALIBRATION

10.2.1. Calibration Ranges:

10.2.1.1. Aroclors 1016/1260 are calibrated using a five-point calibration range. All other Aroclors are calibrated using a single point calibration at the anticipated midpoint of the calibration range. Standards are prepared following the instructions in section 6.2.1.

10.2.1.2. The response factor, defined as the ratio of the area response to the standard concentration, is calculated for three to eight characteristic peaks, which are at least 25% of the height of the largest peak in the Aroclor mixture in each Aroclor at each calibration concentration. The average response factor (if the % RSD across the 5 point range is $<20\%$) or a linear calibration not through the origin (if the correlation coefficient (r1) is $\geq 0.99$) is used for quantitation. Calibration is checked every 12 hours or after every twenty (20) samples, whichever comes first, by injecting a calibration verification standard of Aroclor 1016/1260.

10.2.1.3. The standard five point calibration ranges for Aroclors 1016/1260 are 100, 500, 1000, 1500, and 2500 ng/ml (ppb) with the surrogates TcMX/DCB at 25, 50, 100,

150 and 200 ng/ml (ppb). All other Aroclors employ single point calibration at 1000 ng/ml using three to eight characteristic peaks to develop response factor data.

10.2.1.4. Aroclor Calibration: Inject the five standard Aroclor range to determine the average response factor on each column. Inject all remaining Aroclors as individual solutions to determine response factors for the five characteristic peaks on each column.

10.2.1.5. Generating a calibration table: After the five calibration standards have been run, the data files are copied to the Target Chromatography System. A new Target batch is created and the method file from the previous Target batch is copied to the new Target batch.

10.2.1.6. The data files representing the five levels of calibration also copied to the new Target batch and processed with the method file. The integrations of the five levels are checked for consistency in Target Review.

10.2.1.7. Linear Calibration. Check the percent relative standard deviation (% RSD) of the response factors for each individual peak in the A1016/1260 mix on each column. If the % RSD is less than 20% over its working range for at least 5 peaks in the A1016/1260 mix, the linearity of the range is assumed. Each individual peak's response factor is used for quantitation of all the samples and verification standards. The average of the value calculated for each individual peak is used to report the concentration in the samples.

10.2.1.8. Linear Calibration Using Least Squares Regression. If the % RSD is $>20\%$ for any given compound, a first order linear regression can be applied to the data to calculate the calibration curve and determine sample concentration. If this method is employed, the $r^1$ (Correlation Coefficient) value must be $\geq 0.99$ for the calibration to be acceptable.

10.2.2. Retention Time Windows

10.2.2.1. Retention time windows must be established on each column to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. All gas chromatographs used for pesticides analysis are equipped with electronic pressure control (EPC). The use of EPC results in little retention time variability between analysis. Accordingly, retention time variability for the purpose of retention time window determination for standards analysis is extremely small. The default window option must therefore be employed as follows to accommodate the excellent precision of EPC equipped systems.

10.2.2.2. Obtain the retention time for the characteristic peaks from each Aroclor from the analysis of the midpoint standard for the calibration curve on each column.

10.2.2.3. Establish the center of the retention time window for each characteristic peak and surrogate by using the absolute retention time for each peak and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

10.2.2.4. The absolute retention times of the calibration verification standard are also checked against the retention time window established by the mid-point standard of the initial calibration.

10.2.2.5. Apply the retention time window data in table 1 to each characteristic peak on each column.

10.2.2.6. Calculate absolute retention time windows for each peak and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed

10.2.2.7. Whenever the observed retention time of a surrogate is outside of the established retention time window, the analyst is advised to determine the cause and correct the problem before continuing analyses.

10.2.2.8. New retention time window data must be generated whenever a chromatographic column is changed or a new detector is installed.

10.2.3. Calibration Verification:

10.2.3.1. After the initial calibration range has been analyzed, a verification standard is run on each column to verify the continued validity of the calibration range. This is required every 12 hour shift and is performed after the last sample analyzed within the 12 hour period. The verification standard is chosen as the middle concentration of a calibration range. The verification standard for PCBs is the mid-range Aroclor 1016/1260 standard at 1000ppb.

10.2.3.2. After the data is analyzed, a Continuing Calibration Custom Report is generated from the verification standard's data file using the most recent calibration range from each column. At least five, pre-selected, characteristic peaks between Aroclor 1016/1260 plus surrogates must be checked to verify that the measured concentration in the check standard is within +/- 15%D (difference) or +/- 15% Drift.

10.2.3.3. The retention times for each characteristic peak must be within the pre-established retention windows from the initial calibration on each column. The window must be updated using the retention time of the characteristic peak in the calibration verification as the midpoint of the window.

10.2.3.4. Use the average response factors from the original five-point calibration for quantitative analysis of PCBs identified in field samples.

10.2.3.5. If alternative average or first order regression calibration procedures were used, the average percent difference for all characteristic peaks in the calibration solution must be less than or equal to 15% difference.

10.2.3.6. All characteristic peaks in the standard mixture must be used for the average percent difference determination (alternative average response).

10.2.3.7. Prepare a calibration summary or list indicating which characteristic peaks did not meet the 15% average percent difference criteria for the data package.

10.2.3.8. The percent drift must be calculated if second order linear regression calibration was employed. The percent drift must be ≤15% for each characteristic peak using non-linear calibration verification.

10.2.3.9. If alternative second order regression calibration procedures were used, the average percent drift for all analytes in the calibration solution must be less than or equal to 15%.

10.2.3.10. If none of the calibration techniques are able to achieve criteria, the calibration criteria have failed and recalibration must be performed.

10.2.3.11. At the end of the analysis sequence, a 1000 ng/ml (ppb) Aroclor1016/1260 Mix standard is analyzed on each column. This standard must meet the criteria for calibration verification. This is known as the closing standards.

10.2.3.12. Samples are always quantitated against the average response factor or calibration curve whichever is applicable. Calibration verification standards only check the validity of the calibration range. Calibration verification standards are never used to quantitate samples.

10.2.4. Analytical Sequence

10.2.4.1. Time clock: The 12-hour time clock for PCB commences with the injection of the calibration or calibration verification standard.

10.2.4.2. Analysis Sequence: The automation of G.C. runs is accomplished via the "SEQUENCE" macro of the Chemstation.

Ideal Sequence

Aroclor 1016/1260 1000 ppb Check Standard Mix
Additional Aroclor Check Standards
Blanks and Spike Blanks
QA's (Sample, MS, MSD)
Rush Samples
Remaining Samples
Oil Samples
Aroclor 1016/1260 1000 ppb Check Standard Mix

10.2.4.3. After 12 hours of analysis, an Aroclor continuing calibration verification standard mix must be analyzed. If this "bracket" standard fails criteria, all samples analyzed during the previous period must be re-analyzed. The "bracket" standard must meet all calibration verification criteria.

10.2.4.4. The Sequence File: The sequence file contains the name of Method file corresponding to the type of analysis to be performed, the range of samples to be run, and the number of injections per bottle.

10.2.4.5. It is common practice to run the check standards, evaluate the instrument status, and then complete the Sample Table and Sequence File. If everything else is complete, the run is initiated using the START SEQUENCE soft-key of the SEQUENCE macro.

10.2.5. PCB Data Reporting: The Target Chromatography System calculates the concentrations of the selected Aroclor Peaks. The reporting limit is based on the concentration of the lowest standard in the initial calibration, adjusted for the sample wt/vol, final volume, dilution factor and % moisture (No unqualified

analytical results or non detects may be reported which correspond to an extract concentration less than the lowest standard in the calibration range).

10.2.5.1. The quantitative values for all confirmed analytes must agree within 40%

10.2.5.2. If the quantitative values do not agree within 40%, the discrepancy must be noted in the report with a qualification.

10.3. Documentation

10.3.1. Before the analysis sequence is initiated the GC Performance and Repairs logbook must be filled out. It should contain the following information: date, injector temp, oven temp, detector temp, column A flow, column B flow, signal A, signal B, analysts initials, and notes for any necessary repairs.

10.3.2. After samples have been run, each standard and sample must be entered into the Instrument Run Log. The Instrument Run Log should contain the following information: run date, data file name, vial position, sample number, initial volume/weight, final volume, dilution factor method, job number, QA number, extraction date, lab prep batch, target batch signature of analyst at the bottom of each page, lot numbers for standards used, and result of run (O.K., dilution, non-inject, etc.).

11. QUALITY CONTROL

11.1. Matrix Spikes. On an ongoing basis a matrix spike, matrix spike duplicate and blank spike must be extracted and analyzed on each column for every 20 environmental samples. If the spiked sample recovery results fall outside the laboratory generated limits, the blank spike recovery is evaluated. If the blank spike recovery is within limits the poor sample recovery results are attributed for matrix interference. If the blank spike recovery results are outside QC limits, first the extract is reanalyzed and if it is still outside the limits the entire QA batch must be reextracted and reanalyzed.

11.2. Reagent Blanks. Reagent blanks must be analyzed on each column. The analytical results for reagent blank analysis must fall below the reporting

limit for each compound of interest. If a target compound is detected in the blank at a concentration higher than the reporting limit, first the extract is reanalyzed and if it is still outside the limits the entire batch of samples extracted with the affected blank must be reextracted.

11.3. Surrogate Standards. All sample, blanks and QA samples are spiked with a single component "surrogate" standard (DCB). If the DCB recovery is outside the acceptance range the sample extract is reanalyzed. If the recovery is still outside the limits the sample must be reextracted and reanalyzed or the data flagged as "estimated concentration".

12. CALCULATIONS

See SOP#OC04 for Organic Calculations.

13. METHOD PERFORMANCE

13.1. A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2. All MDL results are available on file.

14. WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. POLLUTION PREVENTION:

14.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15. DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1. Technical acceptance criteria for sample analysis.

15.1.1. The samples must be analyzed on a GC system meeting the initial calibration, continuing calibration and blank technical acceptance criteria.

15.1.2. The sample must be analyzed within the required holding time.

15.1.3. The sample must have an associated method blank meeting the blank technical acceptance criteria.

15.1.4. The percent recovery of each of the system monitoring compounds in the sample must be within the acceptance windows.

15.1.5. The retention time shift for each of the internal standards must be within +/- 0.50 minutes (30 seconds) between the sample and the most recent continuing calibration standard analysis.

15.1.6. After analyzing a sample that exceeds the initial calibration range the analyst must either analyze an instrument blank (using the same

purge inlet if using an auto sampler) which must meet technical acceptance criteria for blank analysis or monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If auto sampler is used, the next sample analyzed using the same purge inlet must also meet the maximum contamination criteria. If the maximum criteria is exceeded then all samples affected by the carryover must be re-analyzed.

15.2. Corrective Action for Sample Analysis

15.2.1. Samples must meet technical acceptance criteria before reporting data.

15.2.2. Corrective action for failure to meet instrument performance checks, initial, continuing calibration and method blanks must be completed prior to sample analysis.

15.2.3. Corrective action for system monitoring compounds and internal standard compounds that fail to meet acceptance criteria must be completed prior to sample analysis.

15.2.4. If any of the system monitoring compounds and internal standard compounds fail to meet acceptance criteria:

- Check all calculations, instrument logs, the system monitoring compound and internal standard compound spiking solutions and the instrument operation. If the calculations were incorrect, correct calculations and verify that the system monitoring compound recoveries and internal standard compound responses meet acceptance criteria.

- If the instrument log for the amount of internal standard compound spiking solution which was added. If an incorrect amount was spiked reanalyze with the correct amount.

- Check the preparation of the internal standards and system monitoring compounds for concentration and expiration.

- Verify that the instrument is operation correctly.

15.2.5. Determine if the problem was a matrix effect.

15.2.6. Check the surrogate recoveries for the MS and MSD.

15.2.7. If the system monitoring compound recoveries and the internal standard compound recoveries meet the acceptance criteria in the reanalyzed samples the samples are considered in control and the data may be reported.

15.2.8. If the system monitoring compound recoveries and the internal standard compound responses do not meet the acceptance criteria in the reanalyzed samples, then submit data from both analyses.

16. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1. Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. Data qualifiers can be found in Appendix A. If applicable, a Corrective Action Reports will be initiated in order to provide for investigation and follow-up.

17. REFERENCES

17.1. United States Environmental Protection Agency, "Method SW8000B: Determinative Chromatographic Separations, Method 8082A Organochlorine Pesticide by Gas Chromatography", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 3, December 1996.

**Table 2**
**Retention Time (RT) Windows for Multicomponent Analytes/Surrogates**

| Compound | RT Window (minutes) |
|---|---|
| Aroclors | ±0.07 |
| 2,4,5,6-Tetrachloro-m-xylene | ±0.05 |
| Decachlorobiphenyl | ±0.10 |

**Table 3**
**Laboratory Generated Spike/RPD/Surrogate Limits**
**(updated annually)**

| Compound | aqueous | rpd | SOX non-aq | rpd | organic | rpd | wipes | rpd |
|---|---|---|---|---|---|---|---|---|
| Aroclor 1016 | 52-156 | 27 | 61-149 | 22 | 69-210 | 8 | 70-130 | 40 |
| Aroclor 1260 | 41-171 | 35 | 61-160 | 21 | 72-222 | 10 | 70-130 | 40 |
| DCB(surr) | 31-135 | | 59-171 | | 48-178 | | 70-130 | |

Sonication Non-aqueous

| | | |
|---|---|---|
| Aroclor 1016 | 70-130 | 40 |
| Aroclor 1260 | 70-130 | 40 |
| DCB(surr) | 70-130 | |

Controlled Copy
Copy No. UNCONTROLLED COPY
Implementation Date: 10/7/05

SOP No.: KNOX-GC-0011
Revision No.: 6
Revision Date: 8/30/05


# STL KNOXVILLE

## STANDARD OPERATING PROCEDURE

## TITLE: Analysis of Polychlorinated Biphenyl Congeners Based on SW-846 Method 8082

## (SUPERSEDES: KNOX-GC-0011, Rev. 4)

Prepared By: Michael S. Patty

Reviewed By: 9/2/05
Technical Specialist

Approved By: 09/02/05
Quality Assurance Manager

Approved By: 9-6-05
Environmental, Health and Safety Coordinator

Approved By: 9-6-05
Laboratory Director

## 1. Scope and Application

1.1. This SOP describes procedures to be used when SW-846 Method 8082 is applied to the analysis of polychlorinated biphenyl (PCB) congeners by gas chromatography/electron capture detection (GC/ECD). It is applicable to extracts derived from any matrix which are prepared according to the sample extraction SOP, KNOX-OP-0014, current revision.

1.2. Table 1 lists compounds that are routinely determined by this method and gives the reporting limits (RL) for each matrix. RLs given are based on the low-level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

## 2. Summary of Method

2.1. This method presents conditions for the analysis of prepared extracts for PCB congeners. The congeners are separated by dual fused silica capillary columns and detected by electron capture detection. Quantitation is performed using the internal standard method.

2.1.1. Aqueous samples are extracted with methylene chloride using continuous liquid / liquid extraction. Solid samples are extracted with methylene chloride/acetone using Soxhlet extraction. Waste dilution is used for samples that are miscible with the solvent.

2.1.2. Extracts are dried and concentrated to a volume of 10 ml. The extracts are then cleaned using a sulfuric acid wash. When necessary, extracts are cleaned using mercury treatment or tetrabutyl ammonium (TBA) sulfite treatment to remove elemental sulfur. Extracts are washed with a 5% NaCl solution, dried and concentrated to final volume using nitrogen evaporation.

2.1.3. After the initial preparation step, the sample is introduced into the GC and concentrations of target analytes are measured by the detector response, within a defined retention time window, relative to the response to standard concentrations.

## 3. Definitions

3.1. Definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.

## 4. Interferences

4.1. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Elemental sulfur, often associated with sediments from sites with anaerobic conditions, may result in analytical signal suppression. Sulfur is removed using mercury cleanup or treatment with TBA sulfite.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including Florisil® cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and sulfur cleanup (Method 3660).

## 5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Specific Safety Concerns or Requirements

5.2.1. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.2.2. There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2.3. Equipment goggles or a face shield **must** be used when employees are using solvents to rinse or clean glassware

5.3. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in**

**the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Hexane | Flammable Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Methylene Chloride | Carcinogen Irritant | 25 ppm-TWA 125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| Mercury | Oxidizer Corrosive Poison | 0.1 Mg/M3 Ceiling (Mercury Compounds) | Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

5.3.1. PCBs have been classified as potential carcinogens under OSHA. Concentrated solutions of PCBs must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.4. Exposure to chemicals will be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. Opened containers of neat standards will be handled in a fume hood.

5.6. Sample extracts and standards that are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.7. When using hydrogen gas as a carrier, all precautions listed in the STL Corporate Safety Manual shall be observed.

## 6. Equipment and Supplies

6.1. An analytical system complete with a gas chromatograph and a $^{63}Ni$ electron capture detector is required. A data system capable of measuring peak area and/or height is required.

6.2. Refer to Table 2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

## 7. Reagents and Standards

7.1. Calibration Standards: A calibration curve with at least five points is prepared at nominal concentrations ranging from 1 to 50 ng/ml for each compound of interest in hexane. Some compounds may be prepared at higher levels due to chromatographic performance, stability, and sensitivity. Refer to Table 3 for analytes and calibration levels.

7.2. Surrogate Standards: A 100 ng/mL surrogate spiking solution is prepared in methanol. Tetrachloro-m-xylene and 2,3,3',5,5',6-Hexachlorobiphenyl (BZ 165) are used as surrogate standards. Refer to Table 3 for the calibration levels for surrogate standards and to Table 4 for the typical spiking levels.

7.3. Internal Standards: A 250 ng/mL internal standard (IS) solution is prepared in hexane. Compounds in the IS solution are 2,4,5-Trichlorobiphenyl (BZ 29) and 2,3,3',4,5,6-Hexachlorobiphenyl (BZ 160). Internal standards are added to all standards and extracts at 25 ng per mL of extract. For example, if the volume of an extract used is 100 µL, 10 µL of the 250 ng/mL internal standard solution would be added. Refer to Table 3.

7.4. Quality Control (QC) Standards: The LCS and MS/MSD spiking solution is prepared to contain a final concentration of 100 ng/mL for all analytes except BZ1, BZ3 and BZ15. The concentrations of BZ1 and BZ3 are 2000 ng/mL and the concentration of BZ15 is 500 ng/mL. Refer to Table 4 for typical spiking levels.

7.5. Initial Calibration Verification Standard (2nd Source Standard): The mid level ICV standard includes all analytes. The standard is prepared from a stock independent from the calibration standards.

7.6. The standards listed in sections 7.1 to 7.5 are stored at $\leq 6^{\circ}C$. All standards must be protected from light. Standard solutions must be brought to room temperature before using.

7.6.1. Expiration times for all standards are measured from the time the standard is prepared or one year from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date, then that date is used.

7.6.2. Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standard solutions must be replaced or demonstrated to be valid by comparison to a second source standard after one year.

7.6.3. Calibration standards, ICV standards and spiking solutions are prepared as dilutions of the stock standards. The standards must be replaced or demonstrated to be valid by comparison to a second source standard after six months.

## 8. Sample Collection, Preservation and Storage

8.1. Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log In of Commercial Samples, current revision.

8.2. Extracts must be refrigerated at $\leq 6^{\circ}C$ and should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.3. Water samples are extracted within seven days of sampling and the extracts are analyzed within 40 days of the end of the extraction.

8.4. Solids and waste samples are extracted within fourteen days of sampling and the extracts are analyzed within 40 days of the end of the extraction.

## 9. Quality Control

9.1. Initial Demonstration of Capability: The initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.2. Batch Definition: Batches are defined at the sample preparation stage. Batches should be kept together through the entire analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC Program document (QA-003) for further details of the batch definition.

9.2.1. Quality Control Batch: The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same

time period. The Quality Control batch must contain a matrix spike/matrix spike duplicate (MS/MSD), a laboratory control sample (LCS) and a method blank. Laboratory generated QC samples (blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. Upon client request, the MS/MSD may be replaced with a matrix spike and a sample duplicate. If insufficient sample is available for a MS/MSD, a LCS duplicate may be substituted.

9.3. Control Limits: In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples. These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless those limits are tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.3.1. These limits do not apply to dilutions greater than 5X. Surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All surrogate, LCS, and MS recoveries must be entered into QuantIMS so that accurate historical control limits can be generated.

9.3.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.4. Surrogates

9.4.1. Every sample, blank and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 4.

9.4.2. If only one surrogate in a sample extract is outside the control limit, and all of the method blank and LCS surrogates and spikes are in control, the outlier may be attributed to matrix effects. For work done in support of the DOD QSM, both surrogates must be within limits or the samples must be re-extracted if sufficient sample material is available and if matrix effects have not already been confirmed. The client may be contacted for input if the re-extraction is expected to take place after the sample holding time has been exceeded.

9.4.3. If both sample surrogates are outside limits, the following corrective actions must take place (except for dilutions greater than 5X):

9.4.4. Check all calculations for error.

9.4.5. Ensure that instrument performance is acceptable.

9.4.6. Recalculate the results and/or reanalyze the extract if either of the above checks reveal a problem.

9.4.7. If none of the above resolves the problem, reprepare and reanalyze the sample or flag the data as "Estimated Concentration". Repreparation is not necessary if there is an obvious chromatographic interference.

Note: The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to a matrix effect (unless the analyst believes that the repeated out of control results are not due to a matrix effect).

9.4.8. If dual column analysis is used, the choice of which result to report is made in the same way as for the samples (Section 12.2.2) unless one column is out of control, in which case the in-control result is reported.

9.4.9. If the surrogates are out of control for the original sample, MS and MSD, then a matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

9.4.10. Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.5. Method Blanks

9.5.1. For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous samples, and reagent sand and sodium sulfate for soil samples (refer to SOP KNOX-OP-0014 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The concentration of any target analyte must be less than the RL in the method blank and meet the following acceptance criteria: (Note: For work done in support of the DOD QSM, the concentration of any target analytes must be $\leq$ ½ the RL, and the samples must be reported to the MDL unless otherwise specified by the client.)

9.5.1.1. If the concentration of a target analyte in the method blank is greater than the MDL but less than the reporting limit, corrective action is required, but the associated data may be reported. The corrective action must include the addition of "B" qualifiers to the results for the associated samples with the corresponding analytes detected in the method blank above the MDL.

9.5.1.2. If the concentration of a target analyte in the method blank is above the reporting limit and the associated sample values are more than 10 times the concentration present in the method blank, corrective action is required, but the associated data may be reported. The corrective action must include the addition of "B" qualifiers to the results for the associated samples with the corresponding analytes detected in the method blank.

9.5.1.3. If the concentration of a target analyte in the method blank is greater than the reporting limit, and the concentration of that analyte in an associated sample is less than 10 times the method blank concentration, the sample batch must be reextracted and reanalyzed.

9.5.1.4. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with a narrative statement that describes the issue.

9.6. Instrument Blanks

9.6.1. An instrument blank must be analyzed prior to sample analysis during any 12 hour period of analysis that does not contain a method blank.

9.6.2. An instrument blank consists of the appropriate solvent with internal standards added.

9.6.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples

9.7.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. The LCS contains the analytes shown in Table 4 and must contain the same analytes as the matrix spike.

9.7.2. If any control analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

9.7.3. Refer to the QC Program document (QA-003) for further details of the corrective action.

9.7.4. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.2.2) unless one column is out of control, in which case the in-control result is reported.

9.8. Matrix Spikes/Matrix Spike Duplicates: A matrix spike and matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. Spiking compounds and levels are given in Table 4. Compare the percent recovery and relative percent difference (RPD) to the laboratory control limits.

9.8.1. If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.

9.8.2. If the recovery for any component is outside QC limits for both the matrix spike/matrix spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

9.8.3. If a matrix spike/matrix spike duplicate is not possible due to limited sample, then a laboratory control sample duplicate should be analyzed.

9.8.4. The matrix spike/matrix spike duplicate must be analyzed at the same dilution as the unspiked sample.

9.8.5. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.2.2) unless one column is out of control, in which case the in-control result is reported.

9.9. STL QC Program: Further details of QC and corrective action guidelines are presented in the QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

## 10. Calibration and Standardization

10.1. Refer to S-Q-004, current revision, Acceptable Manual Integration Practices and the STL Knoxville attachment for information on manual integration practices and documentation requirements.

10.2. Refer to Table 2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table 7. Chromatographic resolution is defined in section 10.10.

10.3. Refer to Table 5 for initial calibration and continuing calibration analytical sequences.

10.4. Refer to Appendix II for a calibration and spike summary.

10.5. Internal standard calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. Prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in Table 3.

10.6. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns or replacing the electron capture detector. A new calibration is not required after clipping the column, replacing the septum or syringe or other minor maintenance.

10.7. With the exception of Section 10.8, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve.

10.8. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Refer to policy P-T-001, current revision, Selection of Calibration Points, for details. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.9. Internal standard calibration

10.9.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected, etc., can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. The internal standards are similar in analytical behavior to the compounds of interest. Typical internal standards are listed in Table 3. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix

interferences (i.e., the magnitude of the internal standard area or height must be within 50 to 150% of the response in the mid-level of the initial calibration). If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. (Refer to SOP KNOX-GC-0015 for the external standard calculations.) In this event, use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.9.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{H_s \times C_{is}}{H_{is} \times C_s}$$

Where:
$H_s$ = Response for the analyte to be measured, height
$H_{is}$ = Response for the internal standard, height
$C_{is}$ = Concentration of internal standard
$C_s$ = Concentration of the analyte to be determined in the standard

10.9.3. Average response factor

The average response factor may be used if the percent relative standard deviation (%RSD) of the response factors is $\leq$ 20%.

The equation for average response factor is:

$$Average\ response\ factor = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: $n$ = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.10. The following requirements must be met for any calibration to be used:

- All analytes must be adequately resolved chromatographically to perform separate integrations for compounds shown as resolved in Table 7. The resolution must be achieved on the highest level standard used in the most recent calibration. Chromatographic resolution is defined as having at least 0.04 minutes between all retention times, and with a distinguishable valley between the two peaks.

- Response must increase with increasing concentration.

10.11. Initial Calibration Verification Standard (2nd Source Standard)

10.11.1. A mid-level standard from a second source is analyzed as the initial calibration verification (ICV). The ICV shall be analyzed with each initial calibration.

10.11.2. The ICV must be within +/- 25% of its expected value with allowance for up to two analytes within +/- 35%.

10.12. Calibration Verification (CCV)

10.12.1. The working calibration curve or RF must be verified by the analysis of a mid point calibration standard (CS-4 or CS-5 in Table 3) at the beginning, after every 12 hours or every 20 samples (including matrix spikes, LCSs and method blanks), whichever is more frequent, and at the end of the analysis sequence. For work done in support of the DOD QSM, the working calibration curve must be verified by the analysis of a mid point calibration standard at the beginning, after every 10 samples and at the end of the analysis sequence. The center of each retention time window may be updated with each calibration verification at the discretion of the analyst.

10.12.2. % Drift calculation

% Drift is used for evaluating calibration verification.

$$\%\ Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.12.3. Any individual compounds with %D $\leq$15% meet the calibration criteria.

10.12.4. It is not necessary to run a daily calibration verification standard (CCV) at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration and second source standard (ICV).

10.12.5. Closing calibration standards are not necessary for internal standard methods.

10.12.6. The internal standard response in a calibration verification standard must be within 50 to 150% of the response in the mid-level of the initial calibration.

10.12.7. If the analyst notes that a CCV failed and can document the reason for failure (e.g., broken vial, carryover from the previous sample, etc.), then a second CCV may be analyzed without any adjustments to the instrument.

10.12.8. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then the laboratory has to demonstrate performance after corrective action with two consecutive successful calibration verifications. If the laboratory has not demonstrated acceptable performance, sample analyses must not occur until a new initial calibration curve is established and verified. However, sample data associated with an unacceptable calibration verification may be reported as qualified data under the following special conditions:

10.12.8.1. When the acceptance criteria for the continuing calibration verification is exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise, the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

10.12.9. If highly contaminated samples are expected, it is acceptable to analyze blanks or primers at any point in the run.

10.12.10. Corrective Action for Samples: For this internal standard method, any samples injected after a standard not meeting the calibration criteria must be reinjected.

## 11. Procedure

11.1. Extraction: The extraction procedure is described in SOP KNOX-OP-0014.

11.2. Cleanup: Appendix III contains instructions for sulfur removal using elemental mercury. Other cleanup procedures are described in SOP KNOX-OP-0014.

11.3. Gas Chromatography: Typical gas chromatographic conditions are given in Table 2.

11.4. Sample Introduction: Analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure. Allow extracts to warm to ambient temperature before injection. Add the internal standard solution to the extract (1:10 ratio).

11.5. Analytical Sequence: An analytical sequence starts with an initial calibration or CCV. The typical analytical sequence is given in Table 5. If there is a break in the analytical sequence of greater than 12 hours, a 12-hour calibration verification standard must be analyzed before proceeding with the sequence.

11.6. Retention Time Windows

11.6.1. Retention time windows must be determined for all analytes. Make three injections of all analytes of interest over the course of a 72 hour period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The centers of the windows are updated with the mid-point of the initial calibration. The windows may also be updated at the discretion of the analyst, on the basis of the12-hour calibration verification.

11.6.3. If the retention time window as calculated above is less than +/- 0.03 minutes, use +/- 0.03 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. The laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times: The retention times of all compounds in each continuing calibration must be within the most recently updated retention time windows. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed.

11.7. Percent Moisture: Analytical results are reported as dry weight. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP KNOX-WC-0012 for determination of percent moisture.

11.8. Procedural Variations: Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA manager. If contractually required, the client shall be notified. The

nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

## 12. Data Analysis and Calculations

12.1. Refer to Appendix IV for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2. Qualitative Identification

12.2.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmation column, at a concentration greater than the reporting limit (MDL if J flag confirmation is required by the client).

**Note**: All NFESC or Navy samples must be reported to the MDL unless otherwise specified by the client.

12.2.2. Dual column quantitation: The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. However, the higher result is reported if any of the following three bulleted possibilities are true:

- There is obvious chromatographic interference on the column with the lower result.
- The continuing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)
- There is no interference and the RPD between the two results is >40%.

12.2.3. If the RPD between the responses on the two columns is greater than 40%, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R1 - R2}{\frac{1}{2}(R1 + R2)} \times 100$$

Where: R=Result

12.3. For work done in support of the DOD QSM: If there is no evidence of chromatographic problems, report the higher result. If there are overlapping peaks causing erroneously high results, then report the non-effected result and document in the case narrative. Results between primary and second column should have an RPD ≤40%. Qualify the result if the RPD >40%.

12.4. Surrogate recovery results are calculated and reported as described in Section 9.4.

12.5. Calibration Range: If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the mid-level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.6. Dilutions: Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits above 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample should be reanalyzed at a dilution targeted to bring the largest hit into the upper half of the calibration range.

12.6.1. Guidance for Dilutions Due to Matrix: If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination.

12.6.2. Reporting Dilutions: The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.7. Interferences: If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.8. Calculations

12.8.1. Internal Standard Calculations Using Calibration Factors

12.8.1.1. Aqueous Samples

$$\text{Concentration (ug/L)} = \frac{H_x \times C_{is} \times V_f \times D_f}{H_{is} \times RF \times V_s} \times \text{Split Factor}$$

Where:

$H_x$ = Response for the analyte in the sample, height
$C_{is}$ = Concentration of internal standard added, ng/mL
$V_f$ = Final volume of extract, mL
$D_f$ = Bench dilution factor
$H_{is}$ = Response of the internal standard, height
RF = Response factor for analyte
$V_s$ = Volume of sample extracted, mL

$$\text{Split Factor} = \frac{\text{Total volume of extract prior to final concentration, mL}}{\text{Volume of extract taken for final concentration, mL}}$$

Example 1: TCX in Aqueous Sample (1000 mL sample extracted and concentrated to 10 mL; no split taken)

$H_x$ = 351,469
$C_{is}$ = 25 ng/mL
$V_f$ = 10 mL
$D_f$ = 2
$H_{is}$ = 151,548
RF = 1.706843
$V_s$ = 1000 mL
Split Factor = 1

$$\frac{351{,}469 \times 25\,\text{ng/mL} \times 10\,\text{mL} \times 2}{151{,}548 \times 1.706843 \times 1000\,\text{mL}} \times 1 = 0.679\ \text{ng/mL (ppb)}$$

Example 2: TCX in Low-level Aqueous Sample (1000 mL sample extracted and concentrated to 10 mL; 5 mL taken and concentrated to 0.5 mL)

$H_x$ = 272,035
$C_{is}$ = 25 ng/mL
$V_f$ = 0.5 mL
$D_f$ = 2
$H_{is}$ = 153,024
RF = 1.706843
$V_s$ = 1000 mL
Split Factor = 10 mL/5 mL

$$\frac{272{,}035 \text{ x } 25\,ng/mL \text{ x } 0.5\,mL \text{ x } 2}{153{,}024 \text{ x } 1.706843 \text{ x } 1000\,mL} \text{ x } \frac{10mL}{5mL} = 0.052\ ng/mL\ (ppb)$$

12.8.1.2. Non-aqueous Samples

$$\text{Concentration}\,(ug/kg) = \frac{H_x \text{ x } C_{is} \text{ x } V_f \text{ x } D_f}{H_{is} \text{ x } RF \text{ x } W_s} \text{ x Split Factor}$$

Where:

$W_s$ = Weight of sample extracted, g

Example 3: TCX in Soil (18.2 g sample extracted and concentrated to 10 mL; no split is taken)

$H_x = 59{,}321$
$C_{is} = 25$ ng/mL
$V_f = 10$ mL
$D_f = 1$
$H_{is} = 152{,}301$
RF = 1.706843
$V_s = 18.2$ g
Split Factor = 1

$$\frac{59{,}321 \text{ x } 25\,ng/mL \text{ x } 10\,mL \text{ x } 1}{152{,}301 \text{ x } 1.706843 \text{ x } 18.2\,g} \text{ x } 1 = 3.13\ ng/g\ (ppb)$$

Note: RLs and MDLs in the QuantIMS reference data are based on extracting 10 g of soil. Therefore, the QuantIMS dilution factor must be used to adjust the RLs and MDLs when a sample weight other than 10 g is extracted.

$$\text{QuantIMS Dilution Factor (DF)} = \frac{10\,g, \text{ nominal weight}}{\text{Actual Weight Extracted, g}} \text{ x Bench dilution factor}$$

Example 4: Actual weight of sample extracted = 18.2 g
Bench dilution factor = 1

$$\text{QuantIMS DF} = \frac{10\,g}{18.2\,g} \text{ x } 1 = 0.549$$

QuantIMS will only accept two decimal places in the dilution factor field, therefore, 0.55 must be entered.

12.8.2. The internal standard response in the samples must be within 50%-150% of the response in the mid-point of the previous ICAL. If the internal standard response is within acceptance criteria on one column, but outside criteria on the second column, the sample results will be reported using the column with acceptable results. If the internal standard response exceeds this criteria on both columns, the following corrective action must be taken:

- Verify that the instrument is working properly.
- Reinject the sample extract.

12.8.3. Surrogate Recovery: Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factors from the initial calibration are used. Surrogate recovery is calculated using the following equation:

$$\%\,\text{Recovery} = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

## 13. Method Performance

13.1. Method Detection Limit: Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. Method Detection limits are determined and verified as specified in the current revision of SOP S-Q-003 (and attachment) based on 40 CFR Part 136 Appendix B. MDL summaries are stored on the local area network.

13.2. Initial Demonstration: Each analyst must complete a successful initial demonstration of capability (IDOC). This requires analysis of QC check samples containing all of the standard analytes for the method.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid-level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table 6.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

## 14. Pollution Prevention

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

## 15. Waste Management

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Expired primary and working PCB standards are stored in metal closed-top containers.
- Vials containing sample extracts are stored in plastic or metal containers resistant to solvents.

## 16. References

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B.

16.2. SW846, Update III, December 1996, Method 8082.

16.3. STL Quality Management Plan (QMP), current revision.

16.4. STL Knoxville Laboratory Quality Manual (LQM), current revision.

16.5. S-Q-004, Acceptable Manual Integration Practices and the STL Knoxville Attachment, current revision.

## 17. Miscellaneous

17.1. Modifications from Reference Method: None

17.2. Appendix I: Tables

17.2.1. Table 1 - Standard Analyte List

17.2.2. Table 2 - Gas Chromatographic Conditions

17.2.3. Table 3 – Typical Calibration Levels

17.2.4. Table 4 - Typical OPR, LCS, MS & MSD Spiking Levels

17.2.5. Table 5 - Typical Analytical Sequence

17.2.6. Table 6 - Performance Criteria for Four Replicate Initial Demonstrations of Capability

17.2.7. Table 7 - Resolution with Typical Chromatographic Conditions

17.3. Appendix II: Calibration and Spike Summary

17.4. Appendix III: Sulfur Removal using Elemental Mercury

17.5. Appendix IV: Example Data Review Checklist

**Table 1 Standard Analyte List**

| Analyte | | | Reporting Limit | | | | |
|---|---|---|---|---|---|---|---|
| CAS Number | BZ[1] | Compound Name | Aqueous ug/L | Low-level Aqueous (ug/L) | Solid ug/kg (Dry) | Tissue ug/kg (Total) | Waste ug/kg |
| 2051-60-7 | 1 | 2-Chlorobiphenyl | 0.2 | 0.02 | 20 | 20 | 2000 |
| 2051-62-9 | 3 | 4-Chlorobiphenyl | 0.2 | 0.02 | 20 | 20 | 2000 |
| 16605-91-7 | 5 | 2,3-dichlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 34883-43-7 | 8 | 2,4'-Dichlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 2050-68-2 | 15 | 4,4'-Dichlorobiphenyl | 0.05 | 0.005 | 5 | 5 | 500 |
| 37680-65-2 | 18 | 2,2',5-Trichlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 7012-37-5 | 28 | 2,4,4'-Trichlorobiphenyl | 0.01 | 0.001 | 10 | 10 | 100 |
| 16606-02-3 | 31 | 2,4',5-trichlorobiphenyl | 0.01 | 0.001 | 10 | 10 | 100 |
| 38444-90-5 | 37 | 3,4,4'-Trichlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 41464-39-5 | 44 | 2,2',3,5'-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 70362-45-7 | 45 | 2,2',3,6-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 41464-40-8 | 49 | 2,2',4,5'-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 35693-99-3 | 52 | 2,2',5,5'-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 41464-43-1 | 56 | 2,3,3',4'-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 32598-10-0 | 66 | 2,3',4,4'-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 32598-11-1 | 70 | 2,3',4',5-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 32690-93-0 | 74 | 2,4,4',5-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 32598-13-3 | 77 | 3,3',4,4'-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 70362-50-4 | 81 | 3,4,4',5-Tetrachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-02-8 | 87 | 2,2',3,4,5'-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 68194-07-0 | 90 | 2,2',3,4',5-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38379-99-6 | 95 | 2,2',3,5',6-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-01-7 | 99 | 2,2',4,4',5-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 37680-73-2 | 101 | 2,2',4,5,5'-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 32598-14-4 | 105 | 2,3,3',4,4'-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-03-9 | 110 | 2,3,3',4',6-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 74472-37-0 | 114 | 2,3,4,4',5-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 74472-38-1 | 115 | 2,3,4,4',6-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 31508-00-6 | 118 | 2,3',4,4',5-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 56558-17-9 | 119 | 2,3',4,4',6-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 65510-44-3 | 123 | 2,3',4,4',5'-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 57465-28-8 | 126 | 3,3',4,4',5-Pentachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-07-3 | 128 | 2,2',3,3',4,4'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-05-1 | 132 | 2,2',3,3',4,6'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 35065-28-2 | 138 | 2,2',3,4,4',5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52712-04-6 | 141 | 2,2',3,4,5,5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 51908-16-8 | 146 | 2,2',3,4',5,5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-04-0 | 149 | 2,2',3,4',5',6-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-63-5 | 151 | 2,2',3,5,5',6-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 35065-27-1 | 153 | 2,2',4,4',5,5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 38380-08-4 | 156 | 2,3,3',4,4',5-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 69782-90-7 | 157 | 2,3,3',4,4',5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 74472-42-7 | 158 | 2,3,3',4,4',6-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-72-6 | 167 | 2,3',4,4',5,5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 59291-65-5 | 168 | 2,3',4,4',5',6-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 32774-16-6 | 169 | 3,3',4,4',5,5'-Hexachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 35065-30-6 | 170 | 2,2',3,3',4,4',5-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |

**Table 1 Standard Analyte List, continued**

| Analyte | | | Reporting Limit | | | | |
|---|---|---|---|---|---|---|---|
| CAS Number | BZ[1] | Compound Name | Aqueous ug/L | Low-level Aqueous (ug/L) | Solid ug/kg (Dry) | Tissue ug/kg (Total) | Waste ug/kg |
| 38411-25-5 | 174[2] | 2,2',3,3',4,5,6'-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-70-4 | 177 | 2,2',3,3',4,5',6'-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 35065-29-3 | 180 | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-69-1 | 183 | 2,2',3,4,4',5',6-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 74472-48-3 | 184 | 2,2',3,4,4',6,6'-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-68-0 | 187 | 2,2',3,4',5,5',6-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 39635-31-9 | 189 | 2,3,3',4,4',5,5'-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 41411-64-7 | 190 | 2,3,3',4,4',5,6-Heptachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 35694-08-7 | 194 | 2,2',3,3',4,4',5,5'-Octachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-78-2 | 195 | 2,2',3,3',4,4',5,6-Octachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 40186-71-8 | 200 | 2,2',3,3',4,5',6,6'-Octachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-75-9 | 201 | 2,2',3,3',4,5,5',6'-Octachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 2136-99-4 | 202[2] | 2,2',3,3',5,5',6,6'-Octachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 40186-72-9 | 206 | 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-79-3 | 207 | 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 52663-77-1 | 208 | 2,2',3,3',4',5,5',6,6'-Nonachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |
| 2051-24-3 | 209 | 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl | 0.01 | 0.001 | 1 | 1 | 100 |

[1] PCB congener number originally assigned by Ballschmiter & Zell ("BZ Number"), 1980. (K. Ballschmiter and M. Zell. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fresenius Z. Anal. Chem. 302:20-31. 1980.)

[2] PCB 174 and 202 coelute.

**Table 2 Gas Chromatographic Conditions**

| Parameter | Recommended Conditions |
|---|---|
| Injection Port Mode | Pulse Split: 40 psi for 0.25 min |
| Injection Port Temperature | 250°C |
| Detector Temperature | 330°C |
| Column Temperature Program | 160°C for 0.25 min, 5°C/min to 210°C, 1°C/min to 215°C, 4°C/min to 270°C, 1 min hold. |
| Column 1 | RTX-CLPesticides, 30m x 0.25mm id, 0.25 µm df, or equivalent |
| Column 2 | RTX-CLPesticides II, 30m x 0.25 mm id, 0.20 µm df, or equivalent |
| Gas Flow Split Ratio | 1/25 |
| Split Vent Flow Rate | 20 mL/min |
| Linear Velocity | 50 cm/sec |
| Column Flow | 1.5 mL/min |
| Injection | 1 µL |
| Carrier Gas | Hydrogen |
| Make-up Gas | Nitrogen |
| Y Splitter Type | Restek or J&W or Supelco glass tee |

**Table 3 Typical Calibration Levels**

| CAS Number | BZ-1993 | Compound Name | CS1 ng/mL | CS2 ng/mL | CS3 ng/mL | CS4 ng/mL | CS5 ng/mL | CS6 ng/mL |
|---|---|---|---|---|---|---|---|---|
| 2051-60-7 | 1 | 2-Chlorobiphenyl | 20 | 40 | 100 | 200 | 500 | 1000 |
| 2051-62-9 | 3 | 4-Chlorobiphenyl | 20 | 40 | 100 | 200 | 500 | 1000 |
| 16605-91-7 | 5 | 2,3-dichlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 34883-43-7 | 8 | 2,4'-Dichlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 2050-68-2 | 15 | 4,4'-Dichlorobiphenyl | 5 | 10 | 25 | 50 | 125 | 250 |
| 37680-65-2 | 18 | 2,2',5-Trichlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 7012-37-5 | 28 | 2,4,4'-Trichlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 16606-02-3 | 31 | 2,4',5-trichlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38444-90-5 | 37 | 3,4,4'-Trichlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 41464-39-5 | 44 | 2,2',3,5'-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 70362-45-7 | 45 | 2,2',3,6-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 41464-40-8 | 49 | 2,2',4,5'-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 35693-99-3 | 52 | 2,2',5,5'-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 41464-43-1 | 56 | 2,3,3',4'-Tetrachlorobiphenyl | 2 | 4 | 10 | 20 | 50 | 100 |
| 32598-10-0 | 66 | 2,3',4,4'-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 32598-11-1 | 70 | 2,3',4',5-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 32690-93-0 | 74 | 2,4,4',5-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 32598-13-3 | 77 | 3,3',4,4'-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 70362-50-4 | 81 | 3,4,4',5-Tetrachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-02-8 | 87 | 2,2',3,4,5'-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 68194-07-0 | 90 | 2,2',3,4',5-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38379-99-6 | 95 | 2,2',3,5',6-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-01-7 | 99 | 2,2',4,4',5-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 37680-73-2 | 101 | 2,2',4,5,5'-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 32598-14-4 | 105 | 2,3,3',4,4'-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-03-9 | 110 | 2,3,3',4',6-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 74472-37-0 | 114 | 2,3,4,4',5-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 74472-38-1 | 115 | 2,3,4,4',6-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 31508-00-6 | 118 | 2,3',4,4',5-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 56558-17-9 | 119 | 2,3',4,4',6-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 65510-44-3 | 123 | 2,3',4,4',5'-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 57465-28-8 | 126 | 3,3',4,4',5-Pentachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-07-3 | 128 | 2,2',3,3',4,4'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-05-1 | 132 | 2,2',3,3',4,6'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 35065-28-2 | 138 | 2,2',3,4,4',5'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52712-04-6 | 141 | 2,2',3,4,5,5'-hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 51908-16-8 | 146 | 2,2',3,4',5,5'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-04-0 | 149 | 2,2',3,4',5',6-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-63-5 | 151 | 2,2',3,5,5',6-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 35065-27-1 | 153 | 2,2',4,4',5,5'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 38380-08-4 | 156 | 2,3,3',4,4',5-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 69782-90-7 | 157 | 2,3,3',4,4',5'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 74472-42-7 | 158 | 2,3,3',4,4',6-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-72-6 | 167 | 2,3',4,4',5,5'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 59291-65-5 | 168 | 2,3',4,4',5',6-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 32774-16-6 | 169 | 3,3',4,4',5,5'-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 35065-30-6 | 170 | 2,2',3,3',4,4',5-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |

| Table 3 Typical Calibration Levels, continued | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| CAS Number | BZ-1993 | Compound Name | CS1 ng/mL | CS2 ng/mL | CS3 ng/mL | CS4 ng/mL | CS5 ng/mL | CS6 ng/mL |
| 38411-25-5 | 174[1] | 2,2',3,3',4,5,6'-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-70-4 | 177 | 2,2',3,3',4,5',6'-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 35065-29-3 | 180 | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-69-1 | 183 | 2,2',3,4,4',5',6-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 74472-48-3 | 184 | 2,2',3,4,4',6,6'-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-68-0 | 187 | 2,2',3,4',5,5',6-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 39635-31-9 | 189 | 2,3,3',4,4',5,5'-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 41411-64-7 | 190 | 2,3,3',4,4',5,6-Heptachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 35694-08-7 | 194 | 2,2',3,3',4,4',5,5'-Octachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-78-2 | 195 | 2,2',3,3',4,4',5,6-Octachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 40186-71-8 | 200 | 2,2',3,3',4,5',6,6'-Octachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-75-9 | 201 | 2,2',3,3',4,5,5',6'-Octachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 2136-99-4 | 202[1] | 2,2',3,3',5,5',6,6'-Octachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 40186-72-9 | 206 | 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-79-3 | 207 | 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 52663-77-1 | 208 | 2,2',3,3',4',5,5',6,6'-Nonachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| 2051-24-3 | 209 | 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| **Surrogates** | | | | | | | | |
| 877-09-8 | TCMX | Tetrachloro-m-xylene | 1 | 2 | 5 | 10 | 25 | 50 |
| 74472-46-1 | 165 | 2,3,3',5,5',6-Hexachlorobiphenyl | 1 | 2 | 5 | 10 | 25 | 50 |
| **Internal Stds** | | | | | | | | |
| 15862-07-4 | 29 | 2,4,5-Trichlorobiphenyl | 25 | 25 | 25 | 25 | 25 | 25 |
| 41411-62-5 | 160 | 2,3,3',4,5,6-Hexachlorobiphenyl | 25 | 25 | 25 | 25 | 25 | 25 |

[1] PCB 174 and 202 coelute.

**Table 4 Typical LCS, MS/MSD and Surrogate Spiking Levels**

| CAS Number | BZ | Compound Name | Control Analytes | Aqueous ug/L | Low-level Aqueous ug/L | Solid ug/kg dry | Tissue ug/kg | Waste ng/kg |
|---|---|---|---|---|---|---|---|---|
| 2051-60-7 | 1 | 2-Chlorobiphenyl | | 2.0 | 0.5 | 200 | 200 | 20000 |
| **2051-62-9** | **3** | **4-Chlorobiphenyl** | **Y** | 2.0 | 0.5 | 200 | 200 | 20000 |
| 16605-91-7 | 5 | 2,3-dichlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 34883-43-7 | 8 | 2,4'-Dichlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **2050-68-2** | **15** | **4,4'-Dichlorobiphenyl** | **Y** | 0.50 | 0.125 | 50 | 50 | 5000 |
| **37680-65-2** | **18** | **2,2',5-Trichlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 7012-37-5 | 28 | 2,4,4'-Trichlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 16606-02-3 | 31 | 2,4',5-trichlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38444-90-5 | 37 | 3,4,4'-Trichlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 41464-39-5 | 44 | 2,2',3,5'-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 70362-45-7 | 45 | 2,2',3,6-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 41464-40-8 | 49 | 2,2',4,5'-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **35693-99-3** | **52** | **2,2',5,5'-Tetrachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 41464-43-1 | 56 | 2,3,3',4'-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **32598-10-0** | **66** | **2,3',4,4'-Tetrachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 32598-11-1 | 70 | 2,3',4',5-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 32690-93-0 | 74 | 2,4,4',5-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 32598-13-3 | 77 | 3,3',4,4'-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 70362-50-4 | 81 | 3,4,4',5-Tetrachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38380-02-8 | 87 | 2,2',3,4,5'-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 68194-07-0 | 90 | 2,2',3,4',5-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38379-99-6 | 95 | 2,2',3,5',6-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38379-99-6 | 99 | 2,2',4,4',5-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38380-01-7 | 101 | 2,2',4,5,5'-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 32598-14-4 | 105 | 2,3,3',4,4'-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38380-03-9 | 110 | 2,3,3',4',6-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 74472-37-0 | 114 | 2,3,4,4',5-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 74472-38-1 | 115 | 2,3,4,4',6-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **31508-00-6** | **118** | **2,3',4,4',5-Pentachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 56558-17-9 | 119 | 2,3',4,4',6-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 65510-44-3 | 123 | 2,3',4,4',5'-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 57465-28-8 | 126 | 3,3',4,4',5-Pentachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **38380-07-3** | **128** | **2,2',3,3',4,4'-Hexachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38380-05-1 | 132 | 2,2',3,3',4,6'-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 35065-28-2 | 138 | 2,2',3,4,4',5'-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52712-04-6 | 141 | 2,2',3,4,5,5'-hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 51908-16-8 | 146 | 2,2',3,4',5,5'-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38380-04-0 | 149 | 2,2',3,4',5',6-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-63-5 | 151 | 2,2',3,5,5',6-Hexachlorobiphenyl | Y | 0.10 | 0.025 | 10 | 10 | 1000 |
| **35065-27-1** | **153** | **2,2',4,4',5,5'-Hexachlorobiphenyl** | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 38380-08-4 | 156 | 2,3,3',4,4',5-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 69782-90-7 | 157 | 2,3,3',4,4',5'-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 74472-42-7 | 158 | 2,3,3',4,4',6-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-72-6 | 167 | 2,3',4,4',5,5'-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 59291-65-5 | 168 | 2,3',4,4',5',6-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 32774-16-6 | 169 | 3,3',4,4',5,5'-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 35065-30-6 | 170 | 2,2',3,3',4,4',5-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |

**Table 4 Typical LCS, MS/MSD and Surrogate Spiking Levels, continued**

| CAS Number | BZ | Compound Name | Control Analytes | Aqueous ug/L | Low-level Aqueous ug/L | Solid ug/kg dry | Tissue ug/kg | Waste ng/kg |
|---|---|---|---|---|---|---|---|---|
| 38411-25-5 | 174[1] | 2,2',3,3',4,5,6'-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-70-4 | 177 | 2,2',3,3',4,5',6'-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **35065-29-3** | **180** | **2,2',3,4,4',5,5'-Heptachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-69-1 | 183 | 2,2',3,4,4',5',6-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 74472-48-3 | 184 | 2,2',3,4,4',6,6'-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **52663-68-0** | **187** | **2,2',3,4',5,5',6-Heptachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 39635-31-9 | 189 | 2,3,3',4,4',5,5'-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 41411-64-7 | 190 | 2,3,3',4,4',5,6-Heptachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 35694-08-7 | 194 | 2,2',3,3',4,4',5,5'-Octachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **52663-78-2** | **195** | **2,2',3,3',4,4',5,6-Octachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 40186-71-8 | 200 | 2,2',3,3',4,5',6,6'-Octachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-75-9 | 201 | 2,2',3,3',4,5,5',6'-Octachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 2136-99-4 | 202[1] | 2,2',3,3',5,5',6,6'-Octachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **40186-72-9** | **206** | **2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-79-3 | 207 | 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 52663-77-1 | 208 | 2,2',3,3',4',5,5',6,6'-Nonachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |
| **2051-24-3** | **209** | **2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl** | **Y** | 0.10 | 0.025 | 10 | 10 | 1000 |
| **Surrogates** | | | | | | | | |
| 877-09-8 | TCMX | Tetrachloro-m-xylene | | 0.10 | 0.025 | 10 | 10 | 1000 |
| 74472-46-1 | 165 | 2,3,3',5,5',6-Hexachlorobiphenyl | | 0.10 | 0.025 | 10 | 10 | 1000 |

[1] PCB 174 and 202 coelute.

**Table 5 Typical Analytical Sequence**

| Step Number | Action |
|---|---|
| 1 | Initial Calibration |
| 2 | Initial Calibration Verification |
| 3 | Solvent blank (optional) |
| 4 | Instrument or Method Blank |
| 5 | Up to 20 samples (unless 12 hours comes first) |
| 6 | Solvent blank (optional) |
| 7 | Continuing calibration |
| 8 | Instrument or Method Blank |
| 9 | Up to 20 samples (unless 12 hours comes first) |
| | Repeat steps 7-9 as needed |
| 10 | Instrument or Method Blank |
| 11 | Up to 20 samples (unless 12 hours comes first) |
| 12 | Solvent blank (optional) |
| 13 | Continuing calibration |
| 14 | Instrument or Method Blank |
| 15 | Up to 20 samples unless 12 hours comes first) |
| | Repeat steps 13-15 as needed |

**Table 6 Performance Criteria for Four Replicate Initial Demonstrations of Capability**

| CAS Number | BZ | Compound Name | Mean Recovery Limits | RSD Limit |
|---|---|---|---|---|
| 2051-60-7 | 1 | 2-Chlorobiphenyl | 50-130 | 30 |
| 2051-62-9 | 3 | 4-Chlorobiphenyl | 60-140 | 30 |
| 16605-91-7 | 5 | 2,3-Dichlorobiphenyl | 60-140 | 30 |
| 34883-43-7 | 8 | 2,4'-Dichlorobiphenyl | 60-140 | 30 |
| 2050-68-2 | 15 | 4,4'-Dichlorobiphenyl | 60-140 | 30 |
| 37680-65-2 | 18 | 2,2',5-Trichlorobiphenyl | 60-140 | 30 |
| 7012-37-5 | 28 | 2,4,4'-Trichlorobiphenyl | 60-140 | 30 |
| 16606-02-3 | 31 | 2,4',5-Trichlorobiphenyl | 60-140 | 30 |
| 38444-90-5 | 37 | 3,4,4'-Trichlorobiphenyl | 60-140 | 30 |
| 41464-39-5 | 44 | 2,2',3,5'-Tetrachlorobiphenyl | 60-140 | 30 |
| 70362-45-7 | 45 | 2,2',3,6-Tetrachlorobiphenyl | 60-140 | 30 |
| 41464-40-8 | 49 | 2,2',4,5'-Tetrachlorobiphenyl | 60-140 | 30 |
| 35693-99-3 | 52 | 2,2',5,5'-Tetrachlorobiphenyl | 60-140 | 30 |
| 41464-43-1 | 56 | 2,3,3',4'-Tetrachlorobiphenyl | 60-140 | 30 |
| 32598-10-0 | 66 | 2,3',4,4'-Tetrachlorobiphenyl | 60-140 | 30 |
| 32598-11-1 | 70 | 2,3',4',5-Tetrachlorobiphenyl | 60-140 | 30 |
| 32690-93-0 | 74 | 2,4,4',5-Tetrachlorobiphenyl | 60-140 | 30 |
| 32598-13-3 | 77 | 3,3',4,4'-Tetrachlorobiphenyl | 60-140 | 30 |
| 70362-50-4 | 81 | 3,4,4',5-Tetrachlorobiphenyl | 60-140 | 30 |
| 38380-02-8 | 87 | 2,2',3,4,5'-Pentachlorobiphenyl | 60-140 | 30 |
| 68194-07-0 | 90 | 2,2',3,4',5-Pentachlorobiphenyl | 60-140 | 30 |
| 38379-99-6 | 95 | 2,2',3,5',6-Pentachlorobiphenyl | 60-140 | 30 |
| 38380-01-7 | 99 | 2,2',4,4',5-Pentachlorobiphenyl | 60-140 | 30 |
| 37680-73-2 | 101 | 2,2',4,5,5'-Pentachlorobiphenyl | 60-140 | 30 |
| 32598-14-4 | 105 | 2,3,3',4,4'-Pentachlorobiphenyl | 60-140 | 30 |
| 38380-03-9 | 110 | 2,3,3',4',6-Pentachlorobiphenyl | 60-140 | 30 |
| 74472-37-0 | 114 | 2,3,4,4',5-Pentachlorobiphenyl | 60-140 | 30 |
| 74472-38-1 | 115 | 2,3,4,4',6-Pentachlorobiphenyl | 60-140 | 30 |
| 31508-00-6 | 118 | 2,3',4,4',5-Pentachlorobiphenyl | 60-140 | 30 |
| 56558-17-9 | 119 | 2,3',4,4',6-Pentachlorobiphenyl | 60-140 | 30 |
| 65510-44-3 | 123 | 2,3',4,4',5'-Pentachlorobiphenyl | 60-140 | 30 |
| 57465-28-8 | 126 | 3,3',4,4',5-Pentachlorobiphenyl | 60-140 | 30 |
| 38380-07-3 | 128 | 2,2',3,3',4,4'-Hexachlorobiphenyl | 60-140 | 30 |
| 38380-05-1 | 132 | 2,2',3,3',4,6'-Hexachlorobiphenyl | 60-140 | 30 |
| 35065-28-2 | 138 | 2,2',3,4,4',5'-Hexachlorobiphenyl | 60-140 | 30 |
| 52712-04-6 | 141 | 2,2',3,4,5,5'-Hexachlorobiphenyl | 60-140 | 30 |
| 51908-16-8 | 146 | 2,2',3,4',5,5'-Hexachlorobiphenyl | 60-140 | 30 |
| 38380-04-0 | 149 | 2,2',3,4',5',6-Hexachlorobiphenyl | 60-140 | 30 |
| 52663-63-5 | 151 | 2,2',3,5,5',6-Hexachlorobiphenyl | 60-140 | 30 |
| 35065-27-1 | 153 | 2,2',4,4',5,5'-Hexachlorobiphenyl | 60-140 | 30 |
| 38380-08-4 | 156 | 2,3,3',4,4',5-Hexachlorobiphenyl | 60-140 | 30 |
| 69782-90-7 | 157 | 2,3,3',4,4',5'-Hexachlorobiphenyl | 60-140 | 30 |
| 74472-42-7 | 158 | 2,3,3',4,4',6-Hexachlorobiphenyl | 60-140 | 30 |
| 52663-72-6 | 167 | 2,3',4,4',5,5'-Hexachlorobiphenyl | 60-140 | 30 |
| 59291-65-5 | 168 | 2,3',4,4',5',6-Hexachlorobiphenyl | 60-140 | 30 |
| 32774-16-6 | 169 | 3,3',4,4',5,5'-Hexachlorobiphenyl | 60-140 | 30 |
| 35065-30-6 | 170 | 2,2',3,3',4,4',5-Heptachlorobiphenyl | 60-140 | 30 |

**Table 6 Performance Criteria for Four Replicate Initial Demonstrations of Capability, continued**

| CAS Number | BZ | Compound Name | Mean Recovery Limits | RSD Limit |
|---|---|---|---|---|
| 38411-25-5 | 174 | 2,2',3,3',4,5,6'-Heptachlorobiphenyl | 60-140 | 30 |
| 52663-70-4 | 177 | 2,2',3,3',4,5',6'-Heptachlorobiphenyl | 60-140 | 30 |
| 35065-29-3 | 180 | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 60-140 | 30 |
| 52663-69-1 | 183 | 2,2',3,4,4',5',6-Heptachlorobiphenyl | 60-140 | 30 |
| 74472-48-3 | 184 | 2,2',3,4,4',6,6'-Heptachlorobiphenyl | 60-140 | 30 |
| 52663-68-0 | 187 | 2,2',3,4',5,5',6-Heptachlorobiphenyl | 60-140 | 30 |
| 39635-31-9 | 189 | 2,3,3',4,4',5,5'-Heptachlorobiphenyl | 60-140 | 30 |
| 41411-64-7 | 190 | 2,3,3',4,4',5,6-Heptachlorobiphenyl | 60-140 | 30 |
| 35694-08-7 | 194 | 2,2',3,3',4,4',5,5'-Octachlorobiphenyl | 60-140 | 30 |
| 52663-78-2 | 195 | 2,2',3,3',4,4',5,6-Octachlorobiphenyl | 60-140 | 30 |
| 40186-71-8 | 200 | 2,2',3,3',4,5',6,6'-Octachlorobiphenyl | 60-140 | 30 |
| 52663-75-9 | 201 | 2,2',3,3',4,5,5',6'-Octachlorobiphenyl | 60-140 | 30 |
| 2136-99-4 | 202 | 2,2',3,3',5,5',6,6'-Octachlorobiphenyl | 60-140 | 30 |
| 40186-72-9 | 206 | 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl | 60-140 | 30 |
| 52663-79-3 | 207 | 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl | 60-140 | 30 |
| 52663-77-1 | 208 | 2,2',3,3',4',5,5',6,6'-Nonachlorobiphenyl | 60-140 | 30 |
| 2051-24-3 | 209 | 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl | 60-140 | 30 |
| **Surrogates** | | | | |
| 877-09-8 | TCMX | Tetrachloro-m-xylene | NA | 30 |
| 74472-46-1 | 165 | 2,3,3',5,5',6-Hexachlorobiphenyl | NA | 30 |

| Table 7 Resolution with Typical Chromatographic Conditions | | | | |
|---|---|---|---|---|
| CAS Number | BZ | Compound Name | Resolved on Column A | Resolved on Column B |
| 2051-60-7 | 1 | 2-Chlorobiphenyl | Y | Y |
| 2051-62-9 | 3 | 4-Chlorobiphenyl | Y | Y |
| 16605-91-7 | 5 | 2,3-dichlorobiphenyl | N (PCB 8) | Y |
| 34883-43-7 | 8 | 2,4'-Dichlorobiphenyl | N (PCB 5) | Y |
| 2050-68-2 | 15 | 4,4'-Dichlorobiphenyl | Y | Y |
| 37680-65-2 | 18 | 2,2',5-Trichlorobiphenyl | Y | Y |
| 7012-37-5 | 28 | 2,4,4'-Trichlorobiphenyl | Y | Y |
| 16606-02-3 | 31 | 2,4',5-trichlorobiphenyl | Y | Y |
| 38444-90-5 | 37 | 3,4,4'-Trichlorobiphenyl | Y | Y |
| 41464-39-5 | 44 | 2,2',3,5'-Tetrachlorobiphenyl | Y | Y |
| 70362-45-7 | 45 | 2,2',3,6-Tetrachlorobiphenyl | Y | Y |
| 41464-40-8 | 49 | 2,2',4,5'-Tetrachlorobiphenyl | Y | Y |
| 35693-99-3 | 52 | 2,2',5,5'-Tetrachlorobiphenyl | Y | Y |
| 41464-43-1 | 56 | 2,3,3',4'-Tetrachlorobiphenyl | N (PCB 101) | Y |
| 32598-10-0 | 66 | 2,3',4,4'-Tetrachlorobiphenyl | Y | N (PCB 95) |
| 32598-11-1 | 70 | 2,3',4',5-Tetrachlorobiphenyl | Y | Y |
| 32690-93-0 | 74 | 2,4,4',5-Tetrachlorobiphenyl | Y | Y |
| 32598-13-3 | 77 | 3,3',4,4'-Tetrachlorobiphenyl | Y | Y |
| 70362-50-4 | 81 | 3,4,4',5-Tetrachlorobiphenyl | Y | N (PCB 87) |
| 38380-02-8 | 87 | 2,2',3,4,5'-Pentachlorobiphenyl | Y | N (PCB 81) |
| 68194-07-0 | 90 | 2,2',3,4',5-Pentachlorobiphenyl | Y | N (PCB 101) |
| 38379-99-6 | 95 | 2,2',3,5',6-Pentachlorobiphenyl | Y | N (PCB 66) |
| 38380-01-7 | 99 | 2,2',4,4',5-Pentachlorobiphenyl | Y | Y |
| 37680-73-2 | 101 | 2,2',4,5,5'-Pentachlorobiphenyl | N (PCB 56) | N (PCB 90) |
| 32598-14-4 | 105 | 2,3,3',4,4'-Pentachlorobiphenyl | Y | N (PCB 141) |
| 38380-03-9 | 110 | 2,3,3',4',6-Pentachlorobiphenyl | Y | Y |
| 74472-37-0 | 114 | 2,3,4,4',5-Pentachlorobiphenyl | Y | N (PCB 146) |
| 74472-38-1 | 115 | 2,3,4,4',6-Pentachlorobiphenyl | Y | Y |
| 31508-00-6 | 118 | 2,3',4,4',5-Pentachlorobiphenyl | Y | Y |
| 56558-17-9 | 119 | 2,3',4,4',6-Pentachlorobiphenyl | Y | Y |
| 65510-44-3 | 123 | 2,3',4,4',5'-Pentachlorobiphenyl | Y | N (PCB 149) |
| 57465-28-8 | 126 | 3,3',4,4',5-Pentachlorobiphenyl | Y | Y |
| 38380-07-3 | 128 | 2,2',3,3',4,4'-Hexachlorobiphenyl | Y | Y |
| 38380-05-1 | 132 | 2,2',3,3',4,6'-Hexachlorobiphenyl | N (PCB 153) | Y |
| 35065-28-2 | 138 | 2,2',3,4,4',5'-Hexachlorobiphenyl | Y | N (PCB 158) |
| 52712-04-6 | 141 | 2,2',3,4,5,5'-hexachlorobiphenyl | Y | N (PCB 105) |
| 51908-16-8 | 146 | 2,2',3,4',5,5'-Hexachlorobiphenyl | Y | N (PCB 114) |
| 38380-04-0 | 149 | 2,2',3,4',5',6-Hexachlorobiphenyl | Y | N (PCB 123) |
| 52663-63-5 | 151 | 2,2',3,5,5',6-Hexachlorobiphenyl | Y | Y |
| 35065-27-1 | 153 | 2,2',4,4',5,5'-Hexachlorobiphenyl | N (PCB 132) | Y |
| 38380-08-4 | 156 | 2,3,3',4,4',5-Hexachlorobiphenyl | Y | Y |
| 69782-90-7 | 157 | 2,3,3',4,4',5'-Hexachlorobiphenyl | Y | Y |
| 74472-42-7 | 158 | 2,3,3',4,4',6-Hexachlorobiphenyl | Y | N (PCB 138) |
| 52663-72-6 | 167 | 2,3',4,4',5,5'-Hexachlorobiphenyl | Y | Y |
| 59291-65-5 | 168 | 2,3',4,4',5',6-Hexachlorobiphenyl | Y | Y |
| 32774-16-6 | 169 | 3,3',4,4',5,5'-Hexachlorobiphenyl | Y | Y |
| 35065-30-6 | 170 | 2,2',3,3',4,4',5-Heptachlorobiphenyl | N (PCB 190) | N (PCB 201) |

| Table 7 Resolution with Typical Chromatographic Conditions, continued | | | | |
|---|---|---|---|---|
| CAS Number | BZ | Compound Name | Resolved on Column A | Resolved on Column B |
| 38411-25-5 | 174 | 2,2',3,3',4,5,6'-Heptachlorobiphenyl | N (PCB 202) | N (PCB 202) |
| 52663-70-4 | 177 | 2,2',3,3',4,5',6'-Heptachlorobiphenyl | Y | Y |
| 35065-29-3 | 180 | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | Y | Y |
| 52663-69-1 | 183 | 2,2',3,4,4',5',6-Heptachlorobiphenyl | Y | Y |
| 74472-48-3 | 184 | 2,2',3,4,4',6,6'-Heptachlorobiphenyl | Y | Y |
| 52663-68-0 | 187 | 2,2',3,4',5,5',6-Heptachlorobiphenyl | Y | Y |
| 39635-31-9 | 189 | 2,3,3',4,4',5,5'-Heptachlorobiphenyl | Y | Y |
| 41411-64-7 | 190 | 2,3,3',4,4',5,6-Heptachlorobiphenyl | N (PCB 170) | Y |
| 35694-08-7 | 194 | 2,2',3,3',4,4',5,5'-Octachlorobiphenyl | Y | Y |
| 52663-78-2 | 195 | 2,2',3,3',4,4',5,6-Octachlorobiphenyl | N (PCB 207) | Y |
| 40186-71-8 | 200 | 2,2',3,3',4,5',6,6'-Octachlorobiphenyl | Y | Y |
| 52663-75-9 | 201 | 2,2',3,3',4,5,5',6'-Octachlorobiphenyl | Y | N (PCB 170) |
| 2136-99-4 | 202 | 2,2',3,3',5,5',6,6'-Octachlorobiphenyl | N (PCB 174) | N (PCB 174) |
| 40186-72-9 | 206 | 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl | Y | Y |
| 52663-79-3 | 207 | 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl | N (PCB 195) | Y |
| 52663-77-1 | 208 | 2,2',3,3',4',5,5',6,6'-Nonachlorobiphenyl | Y | Y |
| 2051-24-3 | 209 | 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl | Y | Y |
| Surrogates | | | | |
| 877-09-8 | TCMX | Tetrachloro-m-xylene | Y | Y |
| 74472-46-1 | 165 | 2,3,3',5,5',6-Hexachlorobiphenyl | Y | Y |

## Appendix II: Calibration and Spike Summary

| | CS1 | CS2 | CS3 | CS4 | CS5 | CS6 |
|---|---|---|---|---|---|---|
| | ng/mL | ng/mL | ng/mL | ng/mL | ng/mL | ng/mL |
| All BZ except 1,3,15 | 1 | 2 | 5 | 10 | 25 | 50 |
| BZ 15 | 5 | 10 | 25 | 50 | 125 | 250 |
| BZ 1, 3 | 20 | 40 | 100 | 200 | 500 | 1000 |
| | ug/L | ug/L | ug/L | ug/L | ug/L | ug/L |
| **Aqueous** | 0.01 | 0.02 | 0.05 | 0.10 | 0.25 | 0.50 |
| Initial Sample Volume=1000mL | 0.05 | 0.10 | 0.25 | 0.50 | 1.25 | 2.50 |
| Final Extract Volume=10mL | 0.20 | 0.40 | 1.00 | 2.00 | 5.00 | 10.00 |
| | ug/L | ug/L | ug/L | ug/L | ug/L | ug/L |
| **Low-Level Aqueous** | 0.001 | 0.002 | 0.005 | 0.010 | 0.025 | 0.050 |
| Initial Sample Volume=1000mL | 0.005 | 0.010 | 0.025 | 0.050 | 0.125 | 0.250 |
| Final Extract Volume=1mL | 0.020 | 0.040 | 0.100 | 0.200 | 0.500 | 1.000 |
| | ug/kg | ug/kg | ug/kg | ug/kg | ug/kg | ug/kg |
| **Soil 10 g dry weight** | 1 | 2 | 5 | 10 | 25 | 50 |
| Initial Sample Weight=10g dry | 5 | 10 | 25 | 50 | 125 | 250 |
| Final Extract Volume=10mL | 20 | 40 | 100 | 200 | 500 | 1000 |
| | ug/kg | ug/kg | ug/kg | ug/kg | ug/kg | ug/kg |
| **Waste** | 100 | 200 | 500 | 1000 | 2500 | 5000 |
| Initial Sample Weight=0.1g | 500 | 1000 | 2500 | 5000 | 12500 | 25000 |
| Final Extract Volume=10mL | 2000 | 4000 | 10000 | 20000 | 50000 | 100000 |

**LCS, MS/MSD Spike Concentration (ng/mL)**

| | |
|---|---|
| All BZ except 1,3,15 | 100 |
| BZ 15 | 500 |
| BZ 1, 3 | 2000 |

**Aqueous** 1.0 mL x (100/500/2000 ng/mL) / 1000 mL = 0.10/0.50/2.0 ng/mL
**Low-Level Aqueous** 0.25 mL x (100/500/2000 ng/mL) / 1000 mL = 0.025/0.125/0.50 ng/mL
**Soil 10 g dry weight** 1.0 mL x (100/500/2000 ng/mL) / 10.0 g = 10/50/200 ng/g dry weight
**Waste** 1.0 mL x (100/500/2000 ng/mL) / 0.1 g = 1000/5000/20000 ng/g

**Surrogate Standard Concentration (ng/mL)**

| | |
|---|---|
| BZ 165 | 100 |
| Tetrachloro-m-xylene | 100 |

**Surrogate Spike Concentration (ng/mL)**

**Aqueous** 1.0 mL x 100 ng/mL / 1000 mL = 0.10 ng/mL
**Low-Level Aqueous** 0.25 mL x 100 ng/mL / 1000 mL = 0.025 ng/mL
**Soil 10 g dry weight** 1.0 mL x 100 ng/mL / 10.0 g = 10 ng/g dry weight
**Waste** 1.0 mL x 100 ng/mL / 0.1 g = 1000 ng/g

**Appendix III: Sulfur Removal using Elemental Mercury**

Sulfur Removal: Sulfur can be removed using mercury. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

Sulfur Removal with Elemental Mercury:

- **Note:** Use Mercury sparingly in order to minimize exposure and disposal costs.
- Transfer 500-1000 uL of sample extract into a clean Teflon sealed vial.
- Add one to three drops of mercury to the extract vial and seal.
- Shake well for 15-30 seconds, then swirl in a Vortex-Genie™.
- Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.
- If black precipitate forms, sulfur was present. Shake again, then swirl. Transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or screening indicates that the cleanup is complete.
- Properly dispose of the mercury waste.

# Appendix IV: Example Data Review Checklist

**STL Knoxville GC PCB Congeners Initial Calibration Data Review / Narrative Checklist**
**Method 8082, SOP KNOX -GC-0011, Rev. 6**
**Page 1 of 1**

| | | | |
|---|---|---|---|
| **Analysis Date:** | | **Instrument/File ID:** | |
| **2nd Source Verification Filename:** | | | |

| *Review Items* **A. Continuing Calibration** | **Yes** | **No** | **N/A** | **2nd Level** | **If No, why is data reportable?** |
|---|---|---|---|---|---|
| 1. Were at least 5 levels analyzed? | | | | | |
| 2. Were all ICAL standards used for calibration? | | | | | |
| 3. Is low level standard concentration ≤ RL? | | | | | |
| 4. Are all %RSDs ≤ 20% ? | | | | | |
| 5. Was the response factor for each analyte calculated using the correct internal standard? | | | | | |
| 6. Was each run checked for saturation? | | | | | |
| 7. Are all analytes in the highest calibration standard adequately resolved? | | | | | |
| 8. Is integration acceptable and were all manual integrations clearly identified, initialed, dated and reason given? | | | | | Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other |
| 9. Was ICAL method file processed using the correct result files? (Compare peak heights-areas in method file to heights-areas of calibration standards.) | | | | | |
| 10. Is the 2nd source standard within +/- 25 % of the expected value (20% D for DOD QSM)? | | | | | ☐ ≤2 analytes within +/- 35 % of the expected value: _____ |

| **Analyst:** | **Date:** | **2nd Level Reviewer :** | **Date:** |
|---|---|---|---|
| **Comments:** | | **Comments:** | |

## Appendix IV: Example Data Review Checklist, continued

**STL Knoxville GC PCB Congeners Continuing Calibration Data Review / Narrative Checklist**
**Method: 8082 - KNOX-GC-0011 Rev 6**
**Page 1 of 1**

| *Analysis Date:* | | *Sequence ID:* | | *ICAL File ID:* | | *Scanned file verified as correct* ____ |
|---|---|---|---|---|---|---|

| *Review Items*<br>A. Continuing Calibration | Yes | No | NA | 2nd ✔ | If No, why is data reportable? |
|---|---|---|---|---|---|
| 1. Was the *correct ICAL* used for quantitation? | | | | | |
| 2. Were the *same process parameters* used for the CCAL standards and the ICAL? | | | | | |
| 3. Were *CCAL standards* run at proper frequency *(before all samples and after no more than 20 injections/12 hrs of sample analysis; 10 injections between CCVs for DOD QSM)* ? | | | | | |
| 4. Were RTs within *RT windows?* | | | | | |
| 5. Is *%D* for each analyte $\leq$ *15%* for each CCAL (for DOD QSM: or grand mean <15% with no analytes >20%D. All analytes >15% but < 20% will be documented in the project narrative)? | | | | | |
| 6. Are *internal standards* within 50-150% of ICAL midpoint? | | | | | |
| 7. Is integration acceptable and were all manual integrations clearly identified, initaled, dated and reason given? | | | | | Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other |

| Analyst: | Date: | 2nd Level Reviewer : | Date: |
|---|---|---|---|
| Comments: | | Comments: | |

# Appendix IV: Example Data Review Checklist, continued

**STL Knoxville GC PCB Congeners Data Review / Narrative Checklist LOT #_____**
**Method: 8082, SOP: KNOX-GC-0011 Rev. 6** **Page 1 of 1**

| | | | | | | |
|---|---|---|---|---|---|---|
| Sequence No.: | | | | | | |
| Scanned File: | | | | | | |
| | | | | | | |
| | | | | | | |

| *Review Items* A. Continuing Calibration (CCAL) | Yes | No | N/A | 2nd √ | If No, why is data reportable? |
|---|---|---|---|---|---|
| 1. CCAL Checklist completed for each analytical batch? | | | | | |
| **B. Client Sample and QC Sample Results** | | | | | |
| 1. Were all special project requirements met? | | | | | |
| 2. Were Turbochrom sample IDs, DFs, prep factors verified? | | | | | |
| 3. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples and NCM#:* _____ | | | | | ☐ *[ht1] HT expired upon receipt.*<br>☐ *[ht2] Client requested analysis after HT expired.**<br>☐ **Re-extraction done after HT expired.** |
| 4. Same process file used for samples and ICAL? ($2^{nd}$ Level - Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF or curve.) | | | | | |
| 5. Are sample and MS/MSD surrogates within QC limits? | | | | | ☐ [sur1] MS/MSD surr.%R showed same effect.<br>☐ [sur2] Re-extraction demonstrated same effect.<br>☐ **[sur3] Not enough sample for re-extraction.**<br>☐ [sur7] Obvious matrix interference.<br>☐ **[sur12] Surr.%R high and all targets ND.**<br>☐ **[sur16] 1 Surr. out, but blank & LCS surrogates in control - matrix effect.** |
| 6. Are internal standards within 50-150% of ICAL midpoint? | | | | | |
| 7. Do positive hits meet identification criteria? (RT and 2nd column confirmation for single peak analytes) | | | | | |
| 8. Are positive results within calibration range? | | | | | |
| 9. Were peaks checked for saturation? | | | | | |
| 10. Were integrations acceptable and are all manual integrations clearly identified, initialed, dated and reason given? | | | | | Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other |
| 11. Is largest analyte diluted to 20-100% of the calibration range? | | | | | ☐ [dil1] Dilution required to prevent contamination of instrument due to non-target compounds. |
| 12. Were runs checked for carryover? | | | | | |
| 13. Were soil results calculated using the dry sample weight? | | | | | |
| 13. Final report acceptable? (Results correct, RLs calculated correctly, units correct, surrogate %R correct, appropriate flags used, deviations noted in narrative, dilution factor correct, and extraction/ analysis dates correct.) | | | | | |
| **C. Preparation/Matrix QC** | | | | | |
| 1. LCS done per prep batch and all analytes and surrogates within laboratory established QC limits? | | | | | ☐ **[lcs2] Insufficient sample for reanalysis.***<br>☐ **[lcs3] LCS %R high and all analyte(s) were <RL in associated samples.** |
| 2. Method blank done per prep batch, method blank or instrument blank run with each sequence, and all analytes <RL? (all analytes <1/2 RL for DOD QSM) | | | | | ☐ **[mb3] No analyte > RL in associated samples.***<br>☐ **[mb4] Sample results > 20x higher than blank.**<br>☐ **[mb5] Insufficient sample for reanalysis.*** |
| 3. Method blank surrogate recoveries within QC limits? | | | | | ☐ **[mb1] Sample surrogates OK and there is no analyte >RL in samples associated with blank.*** |
| 4. MS/MSD done per batch? | | | | | ☐ [lcsd] Insufficient sample. LCS/LCSD analyzed. |
| 4. MS/MSD recoveries and RPDs within laboratory generated control limits? | | | | | ☐ [ms1] LCS acceptable - sample matrix effects.<br>☐ [ms2] LCS acceptable. High native analyte concentration relative to spike level.<br>☐ [ms3] Spikes diluted out. LCS acceptable.<br>☐ [rpd] LCS acceptable. RPD out due to lack of sample homogeneity. |
| 5. Were MS run #'s assigned correctly? | | | | | |
| **D. Other** | | | | | |
| 1. Are all nonconformances documented appropriately? | | | | | |

| Analyst: | Date: | $2^{nd}$ Level Reviewer: | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |

* Such action must be taken in consultation with client. GC033R8.DOC, 9/6/05
NOTE: Nonconformance memos are required for **bold** and *italicized* autotext statements: **Bold** = deficiency, *italicized* = anomoly.

Controlled Copy
Copy No. UNCONTROLLED COPY

SOP No.: KNOX-ID-0013
Revision No.: 4
Revision Date: 09/21/05
Implementation Date: 9/22/05


# STL KNOXVILLE

## STANDARD OPERATING PROCEDURE

## TITLE: Analysis of Polychlorinated Biphenyl (PCB) Isomers by Isotope Dilution HRGC/HRMS

## (SUPERSEDES: KNOX-ID-0013, Revision 3)

Prepared By: _____ 9/22/05

Reviewed By: _____ Technical Specialist 9/22/05

Approved By: _____ Quality Assurance Manager 09/22/05

Approved By: _____ Environmental, Health and Safety Coordinator 9-22-05

Approved By: _____ Laboratory Director 9-22-05

Proprietary Information Statement:

This documentation has been prepared by Severn Trent Laboratories (STL) solely for STL's own use and the use of STL's customers in evaluating its qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to STL upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use if for any other purpose other than that for which it was specifically provided. The user also agrees that where consultants or other outside parties are involved in the evaluation process, access to these documents shall not be given to said parties unless those parties also specifically agree to these conditions.

## 1 Scope and Application

1.1 This procedure is designed to meet analytical program requirements where HRGC/HRMS analysis of polychlorinated biphenyl (PCB) isomers is specified. The procedure is used by STL Knoxville for the detection and quantitative measurement of all 209 PCB isomers in a variety of environmental matrices at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. This procedure is based on EPA method 1668A.

1.2 The compounds listed in Table 1 may be determined by this procedure. The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The estimated minimum levels (EMLs) in Table 4 are the levels at which the PCBs can be determined with only common laboratory interferences present. The actual limits of detection and quantitation will vary depending on the complexity of the matrix.

1.3 The Low Calibration Levels (LCL's) of the method are listed in Table 3 for individual isomers. Analysis of a one-tenth aliquot of the sample permits measurements of concentrations up to 10 times the upper calibration range. Samples containing concentrations of PCB's that are greater than ten times the upper calibration are analyzed by protocols designed for such concentration levels.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in section 9.1.

1.5 This procedure is based on "performance-based" methods. These reference methods allow modifications to overcome interferences or lower the cost of measurements, if all performance criteria in the methods are met and method equivalency is established. Deviations from the referenced methods have been incorporated into this procedure and are listed in section 17.1. Deviations to this procedure are only allowed as specified in section 11.1.

1.6 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCBs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

## 2 Summary of Method

2.1 Screening and protocol assignment.

2.1.1 All solid, semi-solid and fish tissue samples are screened by GC/ECD prior to extraction. Aqueous samples may be screened if the potential for congener levels above 40 ng/L exists. Variations to sample size, spiking levels and final volume are established based on the screening result.

2.2 Extraction

2.2.1 Aqueous samples (samples containing less than one percent solids): Stable isotopically labeled analogs of the toxic PCBs plus additional labeled PCB's are spiked into a 1-L sample, and the sample is extracted with methylene chloride using separatory funnel techniques.

2.2.2 Solid and semi-solid (but not tissue): A 1.0 g sub-sample is screened to determine the greatest concentration for individual congeners. Based on the screen, the sample is prepared by one of four protocols. Each protocol defines the sample amount to be extracted, the fraction of the extract to be used, and the final extract volume. Protocol 1 is for samples which can be processed without adjustments for contamination. In this protocol, the labeled compounds are spiked into a sample containing 10 g of solids. The sample is extracted for 16 hours with an appropriate solvent using a Soxhlet extractor. The extract is concentrated for cleanup. If other analyses are to be performed on the same extract, the extract is split and a separate analysis is performed on each extract fraction.

2.2.3 Note: Sample sizes may be adjusted for dry weight or processed as received. The laboratory default is to process as received. The sample amount extracted can be adjusted to a minimum dry weight, if specified in client requirements or a quality assurance summary by the project manager.

2.2.4 Multi-phase samples: Samples containing multiple phases are separated and the phases are extracted following the procedures for the appropriate matrix. The extracts may be combined for cleanup and analysis or processed separately. Specific handling of multi-phase samples should be discussed and documented with the project manager prior to extraction of samples.

2.2.5 Fish and other tissue: A 1.0 g sub-sample is screened to determine the greatest concentration for individual congeners. Based on the screen, the sample is prepared by one of four protocols. Each protocol defines the sample amount to be extracted, the fraction of the extract to be used, and the final extract volume. Protocol 1 is for samples which can be processed without adjustments for contamination. In this protocol, a 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is blended with sodium sulfate, and extracted for 16 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. A portion of the extract is evaporated to dryness and used to determine the lipid content. The remaining extract is concentrated for cleanup.

2.2.6 Non-aqueous liquids such as oils and organic solvents are diluted or solvent exchanged in hexane.

2.3 After extraction, samples may be cleaned up using gel-permeation chromatography, back-extraction with sulfuric acid and Florisil column chromatography.

2.4 After cleanup, the extract is concentrated to either 100 µL or 20 µL. Recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution

(≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.5 An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's.

2.6 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of two ways:

2.6.1 For PCBs with labeled analogs (see Table 1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.

2.6.2 For PCBs without labeled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique.

2.7 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

## 3 Definitions

These definitions and purposes are specific to this method but conform to common usage as much as possible.

Note: Terminology differences existing in some isotope dilution reference methods regarding the functionality of the labeled analogs may lead to confusion. For example, EPA's Office of Solid Waste methods (8280, 8290) use the term "Internal Standards" to describe the labeled analogs which are added to the sample prior to extraction and used to quantitate the native targets. EPA's Office of Water methods (1613B, 1668 Draft) use the term "Labeled Analogs" to describe these same compounds while using the term "Internal Standards" to describe the labeled analogs which are added to the extract just prior to analysis and used to quantitate the recovery of the labeled analogs added before extraction. EPA's Office of Solid Waste methods (8280, 8290) uses the term "Recovery Standards" to describe these later labeled analogs.

The terminology conventions established by the EPA's Office of Solid Waste methods (8280, 8290) are used in the laboratory for all Standard Operating Procedures and internal communications as defined in this section.

3.1 Analyte - A PCB tested for by this method. The analytes are listed in Table 1.

3.2 Calibration standard (CAL) - A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration verification standard (VER) - The mid-point calibration standard (CS3) that is used to verify calibration. See Table 6.

3.4 CB - Chlorinated biphenyl congener. One of the 209 individual chlorinated biphenyl congeners determined using this Method. The 209 CBs are listed in Table 1.

3.5 Cleanup Standard - Isotopically labeled compound that is added to samples, blanks, quality control samples, and calibration solutions. It is added to the samples after extraction but prior to extract cleanup, and is used to judge the efficiency of the cleanup procedures.

3.6 Congener - Any member of a particular homologous series, for example, 2,2'-DiCB.

3.7 CS0.5, CS1, CS2, CS3, CS4, CS5 - See Calibration standards and Table 6.

3.8 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.9 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal having the same retention time as a PCB congener but which does not meet the other qualitative identification criteria defined in the method.

3.10 Estimated Minimum Detection Limit (EMDL) – The lowest concentration at which an analyte can be detected with common laboratory interferences present.

3.11 Estimated Minimum Level (EML) – The lowest concentration at which an analyte can be measured reliably with common laboratory interferences present.

3.12 Field blank - An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.13 GC - Gas chromatograph or gas chromatography.

3.14 Homologous Series - A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.15 HRGC - High resolution GC.

3.16 HRMS - High resolution MS.

3.17 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the Initial calibration to verify the concentration of the Initial Calibration Standards.

3.18 Internal Standards (IS): Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.19 IPR - Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or

instrumentation is modified.

3.20 Isomer - Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 4-DiCB and 9-DiCB are structural isomers.

3.21 Laboratory blank - See Method blank.

3.22 Laboratory control sample (LCS) - See Ongoing precision and recovery standard (OPR).

3.23 Laboratory reagent blank - See Method blank.

3.24 Level of Chlorination (LOC) Congeners – The first and last eluting congeners in each homolog (or level of chlorination). (For the SPB-Octyl Column the LOC Congeners are 1, 3; 4, 15; 19, 37; 54, 77; 104, 126; 155, 169; 188, 189; 202, 205; 208, 206; 209)

3.25 Method blank - An aliquot of a clean test matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.26 Minimum Level (ML) - The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all Method-specified sample weights, volumes, and cleanup procedures have been employed.

3.27 MS - Mass spectrometer or mass spectrometry.

3.28 OPR - Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.29 PAR - Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.30 PFK - Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.31 Primary dilution standard - A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

3.32 Quality control check sample (QCS) - A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.33 PCB - Polychlorinated biphenyl

3.34 Reagent water - Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method minimum level for the analyte.

3.35 Recovery Standard (RS): Isotopically labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

3.36 Relative Percent Difference (RPD): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.37 Relative standard deviation (RSD) - The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3.38 RF - Response factor. See Section 10.3.4.

3.39 RRF - Relative response factor. See Section 10.3.4.

3.40 RSD - See Relative standard deviation.

3.41 SDS - Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials.

3.42 SICP - Selected ion current profile; the line described by the signal at an exact m/z.

3.43 SPE - Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

3.44 Specificity - The ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.45 Stock solution - A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3.46 Surrogate Standards (SS) - Isotopically labeled compounds that are added to XAD samples and calibration solution. They are added to XAD sampling tubes before sampling and are used to measure sampling and recovery efficiency.

3.47 Toxic Congeners (or Toxic Isomers). PCBs determined by the World Health Organization and USEPA to have dioxin-like toxicity. (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189)

3.48 Toxic/LOC Congeners. PCBs belonging to either the Toxic Congeners list, defined in Section 3.47 or the LOC Congeners list, defined in Section 3.24.

3.49 VER - See Calibration verification standard.

3.50 Additional definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.

## 4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse. The non-coplanar PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory at the minimum levels in this method, and baking of glassware in a kiln or furnace at 450 - 500°C may be necessary to remove these and other contaminants.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface. For specific glassware cleaning procedures, see SOP KNOX-QA-0002, current revision, "Glassware Cleaning".

4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory method blanks (section 9.3) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The method blank consists of reagent water for water samples, sand for solid samples, corn oil or fish oil for tissue samples, or reagent solvent for waste samples.

4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCBs are measured by this method, the elimination of interferences is essential. The cleanup steps given in section 11.9 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCBs at the levels shown in Table 3.

4.5 Each piece of reusable glassware is numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Cleanup of tissue - The natural lipid content of tissue can interfere in the analysis of tissue samples for the PCBs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup

procedures used for cleanup of sample extracts. Lipids must be removed by the acid cleanup procedure in section 11.9.3, followed by Florisil (section 11.9.4).

## 5 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile clean room gloves are worn. For operations using solvents that splash, silver shield gloves are recommended. Silver shield gloves protect against breakthrough for most of the solvents used in this procedure

5.3 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.5 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source may be removed from the vacuum manifold through a vacuum interlock.

5.6 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument may be left on.

5.7 When using a scalpel, cut away from yourself. If you are holding something, cut away from your hand.

5.8 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Sulfuric Acid (1) | Corrosive, Oxidizer, Dehydradator | 1 $mg/m^3$ | This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system. |
| Methylene Chloride | Carcinogen, Irritant | 25 ppm-TWA, 125 ppm-STEL | Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin. |
| Hexane | Flammable, Irritant | 500 ppm-TWA | Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes. |
| Methanol | Flammable, Poison, Irritant | 200 ppm-TWA | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| Toluene | Flammable, Poison, Irritant | 200 ppm-TWA<br>*300 ppm-Ceiling* | Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin. |
| Acetone | Flammable | 1000 ppm-TWA | Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. |
| Nonane | Flammable | None established | Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous memebranes and upper respiratory tract. Causes skin irritiation. |
| 2-Propanol | Flammable | 400 ppm -TWA | Flammable liquid and vapor. Harmful if swallowed or inhaled. Causes irritation to eyes and respiratory tract. Affects central nervous system. May be harmful if absorbed through the skin. May cause irritation to the skin. |
| Ethyl Ether | Flammable, Irritant, Peroxide Former | 400 ppm-TWA | General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of with six months.** |

| | | | |
|---|---|---|---|
| Benzene | Flammable, Toxic, Carcinogen | PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL | Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim may experience tightness in the chest, breathlessness, and loss of consciousness. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

5.9 Chemicals that have been classified as **carcinogens**, **potential carcinogens**, or **mutagens include**: benzene, methylene chloride, polychlorinated biphenyls, and toluene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.)

5.10 Chemicals known to be **flammable** are: acetone, benzene, hexane, nonane, tetradecane, and toluene.

5.11 The following materials are known to be **corrosive**: sulfuric acid.

5.12 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.13 The preparation of all standards, reagents, and glassware cleaning procedures that involve solvents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.14 Equipment goggles or a face shield **must** be used when employees are using solvents to rinse or clean glassware

5.15 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.16 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.17 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Benchtops should be covered with plastic backed absorbent paper.

5.18 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.19 Accidents: Remove contaminated clothing immediately, taking precautions not to

contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.20 All work must be stopped in the event of a known or potential compromise to the health or safety of laboratory personnel. The situation must be reported immediately to a laboratory supervisor.

## 6 Equipment and Supplies

Note: All glassware used in extraction and cleanup procedures is solvent rinsed 2 times before use with acetone, methylene chloride and hexane in that order. Pre-extract Soxhlet apparatus with toluene for at least 4 hours. Rerinse the glassware with all 4 solvents once. See SOP KNOX-QA-0002, current revision, "Glassware Cleaning", for details.

6.1 Equipment for sample preparation.

6.1.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.1.2 Tissue homogenizer - Laboratory blender with glass body and stainless steel blades.

6.1.3 Equipment for determining percent moisture.

6.1.3.1 Oven - Capable of maintaining a temperature of 105 ±5°C.

6.1.3.2 Desiccator.

6.1.4 Balances.

6.1.4.1 Top loading - Capable of weighing 10 mg.

6.2 Extraction apparatus.

6.2.1 Liquid/liquid extraction for water samples.

6.2.1.1 Graduated cylinder, 1-L capacity.

6.2.1.2 Separatory funnels, 250-, 500-, and 2000 mL, with fluoropolymer stopcocks.

6.2.2 Soxhlet/Dean-Stark (SDS) extractor for filters and solid/sludge samples.

6.2.2.1 Soxhlet - 50-mm ID, 200-mL capacity with 500-mL round bottom flask.

6.2.2.2 Soxhlet - 64 mm ID, 500-mL capacity with 1000-mL round bottom flask.

6.2.2.3 Glass condenser, capable of fitting top of Soxhlet or Dean Stark apparatus.

6.2.2.4 Thimble - Whatman high purity glass fiber thimbles

6.2.2.5 Dean Stark moisture trap, with fluoropolymer stopcock, to fit Soxhlet.

6.2.2.6 Heating mantles with temperature controls

6.3 Flasks, Erlenmeyer, 500 mL

6.4 Beakers, 500-mL.

6.5 Spatulas - Stainless steel.

6.6 Fluoropolymer squirt bottles, 500 mL

6.7 Filtration apparatus.

6.7.1 Pyrex glass wool – Solvent rinsed.

6.7.2 Glass funnel – 100 mm with short stem.

6.7.3 Buchner funnel – 15-cm.

6.7.4 Glass-fiber filter paper for Buchner funnel above.

6.7.5 Filtration flasks - 1.5- to 2.0-L, with side arm.

6.8 Cleanup apparatus.

6.8.1 Pipettes.

6.8.1.1 Glass, 1 mL, Class A.

6.8.1.2 Borosilicate glass, disposable, Pasteur, 150-mm long x 5-mm ID.

6.8.1.3 Borosilicate glass, disposable, Pasteur, 230-mm long x 5-mm ID.

6.8.1.4 Pipette Bulbs, rubber, disposable.

6.8.1.5 Gel permeation chromatography system (J2 Scientific Accu Prep or equivalent).

6.8.1.6 Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).

6.8.1.7 Chromatographic column: 700 mm x 25 mm ID glass column.

6.8.1.8 Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.

6.8.2 Glass chromatographic columns.

6.8.2.1 All disposable columns are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order). Allow to air dry in a hood.

6.8.3 Oven-For baking and storage of absorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.9 Concentration apparatus.

6.9.1 Nitrogen blowdown apparatus - Rapidvap (Labconco) vented to a fume hood and/or

N-Evap (Organomation Associates, inc., South Berlin, MA), installed in a fume hood.

6.10 Sample vials

6.10.1 Borosilicate glass, 40 mL disposable with fluoropolymer cap

6.10.2 Mini vials, 1.1 mL capacity with a tapered bottom; with Teflon™-faced, rubber septa and screw caps.

6.11 Gas chromatograph - Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.11.1 Column #1 - 30 ±5-m long x 0.25±0.02-mm ID; 0.25-µm film SPB-Octyl (Supelco 2-4218, or equivalent).

6.11.2 Column #2 - 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062 or Restek No.10227) or equivalent.

6.11.3 Column #3 – GC/ECD Screening – 30m X 0.32mm ID X 0.25µm film thickness DB-5 or RTX-5 or equivalent

6.12 Mass spectrometer - Electron impact ionization, shall be capable of repetitively selectively monitoring 20 exact m/z's minimum at high resolution (≥10,000) during a period less than 1.0 second, and shall meet all of the performance specifications in Section 10.

6.13 GC/MS interface - The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.14 Data system - Capable of collecting, recording, and storing MS data.

6.15 GC-ECD system for Sample Screening – Agilent 5890, 6890 or equivalent.

## 7 Reagents and Standards

CAUTION: Refer to Material Safety Data Sheets (MSDS) for specific safety information on chemicals and reagents prior to use or as needed.

CAUTION: During preparation of reagents, associates shall wear lab coat, gloves, safety glasses with side shields, face shield (when using concentrated acid) and laboratory approved shoes as a minimum. Reagents shall be prepared in a fume hood.

7.1 Sulfuric acid - Reagent grade (specific gravity 1.84).

7.2 Sodium chloride - Reagent grade, prepare at 5% (w/v) solution in reagent water.

7.3 Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride, stored in a desiccator, and stored in a pre-cleaned glass bottle

with fluoropolymer lined screw-cap that prevents moisture from entering.

7.4 Purified nitrogen.

7.5 Solvents - Acetone, toluene, n-hexane, 2-propanol, methanol, methylene chloride, ethyl ether and nonane; pesticide quality, from lots that have been approved for use by the Specialty Organics lab.

7.6 Reagent water - Water prepared by passing through carbon bed and ion exchange filters.

7.7 White quartz sand, 60/70 mesh - For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Placed in kiln at a temperature setting of approximately 450c for a minimum of 4 hours.

7.8 Florisil®, Pesticide residue (PR) grade (60/100) mesh; purchased activated at 1250°C (677°F), stored in glass container with fluoropolymer lined top. Fill a clean 1- to 2-L bottle 1/2 to 2/3 full with Florisil® and place in an oven at 125-135 °C for a minimum of 6 hours.

7.9 Perfluorokerosene (PFK) high boiling mass spectroscopy grade; bp 210-260°C; $d^{20}_4$ 1.94; $n^{20}_D$ 1.330; Fluka (Catalog No. - 77275).

7.10 Tetrabutylammonium hydrogen sulfate Sigma Aldrich Cat. No 155837-100g, or equivalent, 97% purity.

7.10.1 Tetrabutylammonium (TBA) sulfite reagent - Prepare the reagent by dissolving 3.39 g of tetrabutylammonium hydrogen sulfate in 100 ml of reagent water. To remove impurities extract this solution three times with 20 ml portions of hexane. After discarding the last hexane wash slowly add 25 g of sodium sulfite to the solution and shake bottle until the sodium sulfite dissolves. Record the date prepared, initials of the preparer and expiration date on the bottle label. This solution can be stored for 1 month at room temperature in an amber bottle with a Teflon-lined lid.

NOTE: To prepare 50 ml of this reagent, halve the recipe listed above.

7.11 Sodium sulfite. Sigma Aldrich Cat. No. 239321-500g or equivalent 98+% purity.

7.12 Standards and Calibration Solutions: Obtained as prepared solutions from Accustandard (New Haven, CT.), Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps.

7.12.1 Native PCB Calibration Stock – Custom PCB Standard containing all 209 congeners used as Certified Reference Standard (Accustandard Product No S-9994-4x). Stock solution purchased at 4 µg/mL in isooctane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with fluoropolymer-lined cap and is used as received.

7.12.2 PCB Congener Mix 1 through 5 standard solutions containing all 209 isomers are Certified Reference Standards (Accustandard Product No's. M-1668A-1, M-1668A-2, M-1668A-3, M-1668A-4, M-1668A-5,). Stock solutions are purchased at 250-750 µg/mL in isooctane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with fluoropolymer-lined cap and is used as received. Initially (while setting up for this method) these five mixes are run in triplicate to determine the retention times for each of the congeners and which congeners will co-elute. The retention times and elution orders listed in Table 11 were confirmed by the analysis of individual congener standards procured from AccuStandard.

7.12.3 209 PCB ICAL Verification stock solution: Prepared by combining the 5 PCB Congener Mixes referred to in section 7.12.2 and diluting to a concentration of 5000-15000 ng/mL in nonane.

7.12.4 Labeled PCB congener solutions used are Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts) and Wellington Laboratories (Guelph, Ontario, Canada). Stock solutions are purchased at 40 µg/mL or 50 µg/mL in nonane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with fluoropolymer-lined cap and is used as received.

7.12.5 Mixed stock standard solutions are prepared by diluting the stock solutions into nonane. The following mixed stock standard solutions are prepared;

7.12.5.1 Native PCB Secondary Stock solution: Prepared by combining the Native PCB Stock solutions referred to in section 7.12.1 and taking to a concentration of 3.0 ug/mL with nonane.

7.12.5.2 13C12 Labeled Internal Standard stock solution: Prepared by diluting the individual stock solutions of the 13C12 labeled internal standards listed in section 7.12.3 and Table 5, to a concentration of 1000 ng/mL in nonane.

7.12.5.3 13C12 Labeled Recovery Standard stock solution: Prepared by mixing the individual stock solutions of the 13C12 labeled recovery standards listed in section 7.12.3 and Table 5, resulting in a concentration of 1000 ng/mL.

7.12.5.4 13C12 Labeled Cleanup Standard Primary Stock solution: Prepared by diluting the individual stock solutions of the 13C12 labeled cleanup standards listed in section 7.12.3 and Table 5, to a concentration of 5000 ng/mL in nonane.

7.12.5.5 13C12 Labeled Surrogate Standard Primary Stock solution: Prepared by diluting the individual stock solutions of the 13C12 labeled surrogate standards listed in section 7.12.3 and Table 5, to a concentration of 5000 ng/mL in nonane.

7.12.6 Calibration Standard solutions (CS0.5 through CS5) are prepared by dilution of the stock standard solution prepared described section 7.12.1 in nonane and labeled stocks

listed in section 7.12.5 . Table 6 shows the calibration solutions components and final concentrations. This series of solutions is used to establish linearity and relative response factors for all compounds in the initial calibration solutions. These RRFs are used to quantify PCB congeners in the calibration verification (VER) and all samples. The CS3 standard is used for calibration verification (VER). The VER solution is used to verify chromatographic performance, and to update retention times and relative retention times.

7.12.7 PAR PCB Spiking Solutions: Prepared by dilution of the stock standard solution prepared described in section 7.12.1 to the concentrations specified in Table 5with acetone in a volumetric flask. 1.0 mL of this solution is added to each IPR or OPR sample prior to extraction. The concentration of this solution is verified by GC/MS before use.

Note: A low concentration PAR PCB spiking solution is prepared at 1 ng/mL for samples to be taken to a final volume of 20 µL (water samples). A high concentration PAR PCB spiking solution is prepared at 5 ng/mL for samples to be taken to 100 µL final volume (other matrices). The analyst must choose the correct solution to use for each sample.

7.12.8 13C12 Labeled Internal Standard Spiking Solutions: Prepared by diluting the 13C12 labeled internal standard stock solution prepared in section 7.12.5.2 to the concentrations specified in Table 5 with acetone in a volumetric flask. 1.0 mL of this solution is added to each sample prior to extraction. The concentration of this solution is verified by GC/MS before use.

Note: A low concentration $^{13}C_{12}$ labeled internal standard spiking solution is prepared at 2 ng/mL for samples to be taken to a final volume of 20 µL (water samples). A high concentration $^{13}C_{12}$ labeled internal standard spiking solution is prepared at 10 ng/mL for samples to be taken to 100 µL final volume (other matrices). The analyst must choose the correct solution to use for each sample.

7.12.9 13C12 Labeled Cleanup Standard Spiking solutions: Prepared by diluting the 13C12 Labeled Cleanup Standard Primary Stock solution prepared in section 7.12.5.4 to the concentrations specified in Table 5 with hexane in a volumetric flask. 1.0 mL of this solution is added to each sample prior to extraction. The concentration of this solution is verified by GC/MS before use.

Note: A low concentration $^{13}C_{12}$ labeled cleanup standard spiking solution is prepared at 2 ng/mL for samples to be taken to a final volume of 20 µL (water samples). A high concentration $^{13}C_{12}$ labeled cleanup standard spiking solution is prepared at 10 ng/mL for samples to be taken to 100 µL final volume (other matrices). The analyst must choose the correct solution to use for each sample.

7.12.10 13C12 Labeled Surrogate Standard Spiking solution: Prepared by diluting the 13C12 Labeled Surrogate Standard Primary Stock solution prepared in section 7.12.5.5 to the concentration specified in Table 5 with nonane in a volumetric flask. 100 uL of this

solution is added to each XAD tube or PUF cartridge prior to sampling. The concentration of this solution is verified by GC/MS before use.

7.12.11 13C12 Labeled Recovery Standard Spiking solution: Prepared by diluting the 13C12 Labeled Recovery Standard Stock solution prepared in section 7.12.5.3 to the concentration specified in Table 5 with nonane in a volumetric flask. Depending upon the required final extract volume, 20uL or 100uL of this solution is added to each sample extract prior to analysis. The concentration of this solution is verified by GC/MS before use.

7.12.12 QC Check Sample - A QC Check Sample should be obtained from a source independent of the calibration standards. This check sample is a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has an SRM 1944 – New York/New Jersey Waterway Sediment that the NYSDEC recommends for use.

7.12.13 Initial Calibration Verification Standard This is a single solution containing all 209 individual PCBs as well as internal standards and recovery standards at the following concentrations:

- mono, di, and tri CBs at 50ng/mL
- tetra, penta, hexa and hepta CBs at 100ng/mL
- octa, nona, and deca CBs at 150ng/mL
- internal standards and recovery standards are at the same concentration as the calibration standards (CS0.5 - CS5)

This solution is always analyzed immediately after the initial calibration.

7.12.13.1 Combine 100 uL of 209 PCB ICAL verification stock solution (Section 7.12.3) (equivalent to 20 uL of each mix) with an 100 uL of the $^{13}C_{12}$ labeled internal standard stock solution (section 7.12.5.2), 100 uL of a 1/10 dilution of the $^{13}C_{12}$ labeled cleanup standard primary stock solution (Section 7.12.5.4), and 100 uL of $^{13}C_{12}$ labeled recovery standard stock solution (Section 7.12.5.3) and 600 uL of nonane to produce the concentrations listed in section 7.12.13.

7.12.13.2 Retention Time Calibration Mixes. These are 5 solutions injected (in triplicate to establish the retention time data referenced in section 10.2.3. Combine 20 uL of the stock specified in section 7.12.2 with an 100 uL of the $^{13}C_{12}$ labeled internal standard stock solution (section 7.12.5.2), 100 uL of a 1/10 dilution of the $^{13}C_{12}$ labeled cleanup standard primary stock solution (section 7.12.5.4), and 100 uL of $^{13}C_{12}$ labeled recovery standard stock solution (section 7.12.5.3) and 600 uL of nonane to produce the concentrations listed in section 7.12.13.

## 8 Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Sample Receipt and Login, current revision.

8.2 Collect samples in amber glass containers following conventional sampling practices.

Note: Sample preservation, if required, must be performed at the time of collection and is the responsibility of the sample collector in accordance with the clients Quality Assurance Project Plan. The methods referenced in section 15 provide sample collection and preservation guidance which may be used in the absence of a specific Quality Assurance Project Plan.

8.3 Sample Storage

8.3.1 Maintain aqueous samples at 0-4°C from the time of collection until receipt at the laboratory. Store aqueous samples in the dark at 0-4°C.

8.3.2 Maintain solid, semi-solid, oily, and mixed-phase, fish, and adipose tissue samples at <4°C from the time of collection until receipt at the laboratory. Fish and adipose tissue should be shipped with dry ice if at all possible. Store solid, semi-solid, oily, and mixed-phase in the dark at <-10°C, store fish, and adipose tissue samples in the dark at <-10°C.

8.4 Holding Times

8.4.1 If stored according to the conditions specified in 8.3, samples may be stored for up to one year.

8.4.2 Store sample extracts in the dark at room temperature until analyzed. If stored in the dark at room temperature, sample extracts may be stored for up to one year.

## 9 Quality Control

9.1 Initial precision and recovery (IPR) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.1 For aqueous samples, extract, clean, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. For solid samples, extract, clean, concentrate, and analyze four aliquots of sand spiked with labeled internal standards and the precision and recovery standard according to the procedures in sections 11. For tissue samples extract, concentrate, clean and analyze four aliquots of corn or other vegetable oil or fish oil spiked with labeled internal standards and the precision and recovery standard according to the procedures in sections 11. All sample processing steps that are to be used for processing samples, including preparation, extraction, and cleanup shall be included in this test.

9.1.2 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the relative standard deviation (RSD) of the concentration in ng/mL for each compound.

9.1.3 For each PCB and labeled compound, compare RSD and X with the corresponding limits for initial precision and recovery in Table 10. If RSD and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual RSD exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 Internal Standards

9.2.1 Every sample, blank, and QC sample is spiked with internal standards. Internal standard recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. When properly applied, results from isotope dilution techniques are independent of recovery. The recovery of each internal standard should be within the limits in Table 10. If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than 25 percent, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDL's) are less than the estimated minimum levels (EML's), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDL's) are greater than the estimated minimum levels (EML's), re-extract and re-analyze the sample. If the ion chromatogram of the PFK lock mass m/z indicates ion suppression in the region where the internal standard elutes, reanalyzing the extract at up to a 1/10 dilution may improve the internal standard recovery. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.2.2 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.3 Method Blanks

9.4 A laboratory method blank must be run along with each analytical batch of 20 or fewer samples. The method blank consists of reagent water for aqueous samples, a clean solid matrix (sand or sodium sulfate) for solid samples, and corn or other vegetable oil or fish oil for tissue samples. Analyze the blank immediately after analysis of the OPR to

demonstrate freedom from contamination. The method blank should not contain any of the compounds of interest at a concentration above the estimated minimum level (EML) shown in Table 4.

9.4.1 Corrective action is required when compounds of interest are detected in the method blank above the EML. Corrective action may include reanalysis of the method blank. Contact the Project Manager to determine further corrective action. At a minimum, all associated results are qualified with a B flag. Re-extraction and reanalysis of all samples associated with a contaminated method blank is required if requested by the client or Project Manager. Investigation of the source of the method blank contamination will be initiated before further samples are extracted.

9.4.2 The method blank must have acceptable internal standard recoveries. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.4.3 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.5 Instrument Blank

9.5.1 Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.6 Ongoing Precision and Recovery (OPR) Sample - An ongoing precision and recovery (OPR) is prepared and analyzed with every batch of 20 samples. All analytes must be within established control limits specified in Table 10. The OPR is spiked with the compounds listed in Table 5.

9.6.1 If any analyte in the OPR is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.
- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints the OPR is reported and the failure is documented in the project narrative.

9.7 QC Check Sample - Analyze the QC Check Sample (section 7.12.12) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least annually.

## 10 Calibration and Standardization

10.1 Three types of calibration procedures are required. The first type establishes retention times, relative retention times and relative retention time windows to be used during the subsequent calibrations and analyses. The second type, initial calibration, is required to establish response factors and is required before any samples are analyzed. It may be required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The third type, continuing calibration, consists of analyzing the continuing calibration verification solution (VER). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.3.7 is demonstrated and documented.

10.2 Retention Time Calibration

Retention time calibration is required if the retention time criteria cannot be met.

10.2.1 Adjust the chromatographic conditions and scan descriptors until the RT and RRT for all congeners are within the windows in Table 2.

10.2.2 The absolute retention time of CB 209 must exceed 55 minutes. Otherwise the GC temperature program must be adjusted and the test repeated until the requirement is met.

Note: When adjusting chromatographic conditions, the resolution requirements of sections 10.3.5.1.2 and 10.3.5.1.3 must be maintained.

10.2.3 Tune the instrument to meet the mass resolution and mass accuracy requirements of section 10.3.2 (for m/z 192.9888 m/z 230.98563, and m/z 280.98243). Document the resolution and accuracy.

10.2.4 Analyze 2µL of each of the five individual PCB mixtures (section 7.12.1). Repeat the series twice more in succession to provide 3 runs of each mix. It is not necessary to interrupt this analytical sequence to perform a 12-hour resolution check. Set the switch-points for the MID descriptors. The switch-points must be set to insure that the first and last eluting isomer of each homolog group and the labeled internal standards are acquired properly. Determine the average retention time of each PCB congener using the elution order information in Table 11.

Note 1: PCB Mixture 5 (M-1668A-5) contains the first and last eluting isomer in each homolog group for the SPB-Octyl column (see Table 7 and Table 11).

Note 2: Laboratory data has indicated that the SPB-Octyl column can exhibit significant differences in performance from column to column. It has also been indicated that the column's performance can change significantly due to oxidation with subsequent changes in congener retention times and elution order. The individual PCB mixtures should be analyzed whenever the column's performance or specific congeners retention times are in doubt.

10.2.5 Calculate the relative retention time for all native and labeled congeners, using their retention time references from Table 2. Calculate the relative retention time for each run in which the congener and its retention time reference are present. (i.e. Three RRTs will be calculated for each native congener. Fifteen RRTs will be calculated for each internal standard.) Use the calculated average retention times for all native and labeled congeners as the RT calibration source in the calculation software.

10.2.6 Calculate the relative retention time window using the absolute retention time windows from Table 2.

$$\text{RRT Limit Low} = \frac{RT_A - (RT_{WIN}/2)}{RT_{IS}}$$

$$\text{RRT Limit High} = \frac{RT_A + (RT_{WIN}/2)}{RT_{IS}}$$

Where

$RT_A$ = Average retention time of analyte

$RT_{IS}$ = Average retention time of RT reference.

$RT_{WIN}$ = Absolute RT window in seconds from Table 2

10.2.7 A single pair of RRT limits is used for all congeners in coeluting set. Use the RRT Limit Low that was calculated for the first eluting congener, and the RRT Limit High calculated for the last eluting congener (in the coelution set).

10.3 Initial Calibration

Initial calibration is required before any samples are analyzed for PCBs. Initial calibration is also required if any continuing calibration (section 10.3.7) does not meet the required criteria in section 10.3.6.

10.3.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 6. Calibration standards should be stored at room temperature and preferably in amber vials. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.3.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). By using a PFK molecular leak, tune the instrument (see the appropriate instrument manufacturer's operating manual for tuning instructions) to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 192.9888 (PFK). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact masses of m/z 230.98563 (PFK) and 280.98243 (PFK) are within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltages of m/z 230.98563 (PFK) and 280.98243 (PFK) are

greater than 10,000 (10 percent valley).

10.3.2.1 Check the resolution and mass accuracy as described above for the following ion sets: m/z 268.98243, 292.98243, 380.97605; 342.97924, 380.97605, 430.97285; 404.97604, 442.97285, 530.96646 (PFK). Iteratively adjust operating parameters and tuning values until the resolution and mass accuracy criteria are met. Document the resolution and mass accuracy for each of the ion sets.

10.3.3 Because of the extensive mass range covered in each function, it may not be possible to maintain 10,000 resolution throughout the mass range during the function. Therefore, resolution must be greater than 8,000 throughout the mass range and must be greater 10,000 in the center of the mass range for each function.

10.3.4 Inject a 2 µL aliquot of the CS0.5 calibration solution.

10.3.4.1 Ion abundance ratios, minimum levels, and signal-to-noise ratios.

10.3.4.1.1 Measure the SICP areas for each congener or congener group, and compute the ion abundance ratios at the exact m/z's specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.

10.3.4.1.2 All Toxic/LOC and labeled compounds in the CS0.5 standard must be within the QC limits in Table 9 for their respective ion abundance ratios; otherwise, the mass spectrometer must be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.3.2) prior to repeat of the test.

10.3.4.1.3 Verify that the HRGC/HRMS instrument meets the estimated minimum levels (EMLs) in Table 4. The peaks representing the CBs and labeled compounds in the CS0.5 calibration standard must have signal-to-noise ratios (S/N) $\geq$ 10; otherwise, the mass spectrometer must be adjusted and this test repeated until the minimum levels in Table 4 are met.

10.3.4.1.4 An exception to the ion abundance ratio and signal to noise ratio requirements is the secondary ion for dichlorinated biphenyls (m/z 223.9974). High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.

10.3.5 Analyze 2µL of each of the other calibration standards.

10.3.5.1 Isomer specificity.

10.3.5.1.1 Use the CS-3 calibration standard to evaluate column performance. The toxic isomers must be uniquely resolved from all other congeners. Isomers may be unresolved so long as they have the same TEF and response factor and so long

as these unresolved isomers are uniquely resolved from all other congeners. For example, the SPB-Octyl column achieves unique GC resolution of all Toxics except congeners with IUPAC numbers 156 and 157. This isomeric pair is uniquely resolved from all other congeners and these congeners have the same TEF and response factor.

10.3.5.1.2 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.3.5.1.3 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.3.5.1.4 Column to column variations in the SPB-Octyl phase significantly affects the resolution of isomers 156 and 157. Document the percent valley between the isomers. If the %valley is < 40% then calculate the isomers as non-coeluting peaks. If the %valley is > 40% then calculate the isomers as co-eluting peaks.

10.3.5.1.5 Classify each congener as resolved or as a member of a coelution set. To be documented as resolved, the valleys between any two isomers must be less than 40 percent of the height of the shorter of the two adjacent peaks. Each member of a coelution set is designated with a qualifier in the format of CXXX, where XXX = the lowest numbered congener in the set. For example, if PCB 156 and PCB 157 coelute, qualify PCB 157 with "C156".

10.3.5.2 Calculate the RRF of each compound of interest (target analytes, coelution sets, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate reference standard
Cis = concentration of the appropriate reference standard
Cs = concentration of the compound of interest

Note: When calculating the RRF for a coelution set, sum the areas of all isomers in the set. Use the resulting RRF for all congeners within the set.

10.3.5.3 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (RSD) of the relative response factors for each compound of

interest in the six calibration standard solutions using the following equations;

$$\overline{RRF}_{n=6} = \frac{1}{n} \times \sum_{i=1}^{n} RF_i$$

$$RSD_{n=6} = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.3.6 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed, otherwise repeat the initial calibration.

10.3.6.1 The percent relative standard deviation (RSD) for the mean relative response factors for the unlabeled native analytes calculated by isotope dilution must not exceed 20 percent. The percent RSD for the mean relative response factors for the unlabeled native analytes calculated by internal standard must not exceed 35 percent. The percent RSD for the mean relative response factors for the labeled standards must not exceed 35 percent.

10.3.7 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.12.13. Calculate the concentration of the ICV using the RRF's from the CS3 standard analyzed in section 10.3.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:

$C_{Exp}$ = The expected concentration of the ICV Standard.
$C_{Calc}$ = The calculated concentration of the ICV Standard.

10.3.7.1 The criteria for acceptance of the ICV Standard are as follows:

- The %D may not exceed ±35% for more than 4 of the native and labeled compounds.
- The %D may not exceed ±50% for any native or labeled compound.

10.3.7.2 All data associated with compounds with percent differences exceeding ±35% must be reviewed before acceptance.

10.3.7.3 All data associated with compounds with percent differences exceeding ±35% shall

be documented as an NCM. Corrective action must be taken and may include the following

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.4 Continuing Calibration

10.4.1 Continuing calibration is performed at the beginning of a 12-hour period after successful mass resolution check.

10.4.2 Document the mass resolution performance as specified in section 10.3.2 at both the beginning and end of the 12-hour period.

10.4.3 Analyze 2µL of the Continuing Calibration Verification Standard (VER). Calculate the concentration (C) of the compounds of interest (target analytes, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation:

$$C = \frac{As \times Cis}{Ais \times RRF}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate reference standard
Cis = concentration of the appropriate reference standard
RRF= mean relative response factor from section 10.3.5.3

10.4.4 Calculate the concentrations as percentages of the test concentrations and compare them to the limits specified in Table 10 using the following equation:

$$C_{ver}\% = \frac{C_{ver}}{C_{test}} \times 100$$

where:

$C_{ver}$ = the concentration of the VER standard calculated in section 10.4.3
$C_{test}$ = the test concentration of the VER standard listed in Table 10.

10.4.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If the acceptance criteria are met the calibration is deemed to be in control and the RRF's generated from the initial calibration are used to quantify samples. If acceptable calibration is not achieved, identify the root cause, perform corrective action, and repeat the

continuing calibration. If a second consecutive attempt at a continuing calibration fails, two consecutive calibrations must meet the criteria, or an initial calibration must be run before proceeding with client samples.

10.4.5.1 The ion abundance ratios of the peaks representing the Toxics/LOCs and labeled standards must be within the control limits specified in Table 9.

10.4.5.2 The S/N for the GC signals present in every SICP (including those for labeled standards) must be ≥ 10.

10.4.5.3 The concentrations calculated as percentages of test concentrations (target analytes, internal standards, cleanup standards, and surrogate standards) must be within the limits in Table 10.

10.4.5.4 For Toxic and LOC congeners, as listed in the first section of Table 10, the percent of the calculated concentration relative to the test concentration must be within 70-130%.

10.4.5.5 For non-Toxics/LOCs the calculated concentrations must be within 40-160% of the test concentrations.

10.4.5.5.1 If the non-Toxic/LOC calculated concentration is within 70-130% of the test concentration, then the ICAL RF for that congener is used. If the calculated concentration is not within 70-130% but is within 40-160%, then calculate the RF from the VER standard for that congener and use it to calculate any associated samples run during that 12 hour shift.

10.4.5.6 The absolute retention times (RT) of the labeled internal standards must be within ±15 seconds of the retention times obtained during initial calibration.

10.4.5.7 The relative retention times (RRT) of the Toxics/LOC congeners must be within their respective RRT limits generated in the retention time calibration in section 10.2.6.

10.4.5.7.1 If the RRT's or RT's are not within the limits above, the GC may not be performing properly. However, routine column maintenance may include removing short amounts of the beginning of the column when active sites or non-volatile compounds in sample extracts cause poor chromatography and loss of specificity. Shortening of the column can cause the RRT's or RT's to fall outside the above limits.

10.4.5.7.2 When the RRT of any compound or the RT of any internal standard is not within the above limits corrective action must be taken. If the GC is not performing properly, correct the problem and repeat the test. If the GC is performing properly but the RRT's or RT's have changed due to routine column maintenance, adjust the GC or replace the GC column, then repeat the test or repeat the retention time calibration.

10.4.5.8 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.4.5.9 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.4.5.10 If PCBs 156 and 157 have been classified as uniquely resolved at the most recent initial calibration, the valley between the two must be less than or equal to 50% the lower of the two peaks. If this cannot be demonstrated, the resolution must be reestablished, or a new initial calibration must be analyzed.

10.4.6 Daily calibration must be performed every 12 hours of instrument operation. The 12-hour shift begins with the documentation of the mass resolution followed by the injection of the Continuing Calibration Standard (VER).

## 11 Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgement of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Samples are extracted by the following procedures depending upon sample matrix. Water samples are prepared by separatory funnel liquid/liquid extraction. Solid samples including soils, sediments, tissues, XAD tubes, PUF cartridges, and solid waste materials are prepared by Soxhlet extraction. Non-aqueous liquid wastes and organic solvents are prepared by waste dilution techniques.

NOTE: Samples should be removed from the refrigerator several hours before extraction and allowed to come to room temperature before measuring the volume or performing the extraction.

11.3 Aqueous Samples (samples containing 1% solids or less.)

11.3.1 Refer to Knoxville SOP, KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware.

11.3.2 Place separatory funnels, one for each sample, in the rings attached to the latticework set up in the hood.

11.3.3 Place the 600 mL Rapid-Vap concentrator tube directly beneath the separatory funnel.

11.3.4 Plug the glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the

funnel stops dripping, place the funnel on top of the flask that is fitted with a paper clip to aid in filtering.

11.3.5 Inspect the sample for solids or biphasic sample characteristics. If either condition exists, consult the project manager for further instructions. Mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. For the method blank and the OPR, use a 1000 mL graduated cylinder to measure 1000 mL of reagent water.

11.3.6 Verify the specified final volume of the extract. If the standard 20 µL is specified, use low-level spiking solutions. Add 1 mL of the low-level $^{13}C$ labeled internal standard spiking solution, specified in section 7.12.8, to the sample. For the IPR or OPR, add 1 mL of the low-level PAR PCB Spiking Solution as specified in section 7.12.7. Record the amount of spike used and the spike standard number in the standards logbook and on the benchsheet.

11.3.7 Add 60 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel. Add 60 mL of methylene chloride to the method blank, LCS/OPR , and LCSD (if required) as well.

11.3.8 Secure the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles may be worn when performing this procedure.

11.3.9 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.3.10 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the concentrator tube. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed. If at least 10 minutes has elapsed and other ways of breaking up or reducing the size of the emulsion have failed the following steps may be tried to reduce the impact of the emulsion on the sodium sulfate.

11.3.10.1 Place a large piece of pre-cleaned glass wool in the funnel containing the sodium sulfate.

11.3.10.2 Spread the glass wool out, covering the entire surface of the sodium sulfate to about a depth of about 5 to 10mm. If the emulsion is hard to break up and persistent, a small, additional layer of sodium sulfate may be added on top of the glass wool.

11.3.10.3 Drain the solvent and emulsion layer into the funnel being careful to drain no more

than 60 mL of volume if a clear phase layer cannot be determined.

11.3.10.4 If this procedure is used the funnel should be rinsed with an extra 30ml of methylene chloride to ensure all analytes are rinsed into the concentrator tube after the third portion of methylene chloride has drained through the sodium sulfate in section 11.3.12.

11.3.11 Repeat steps 11.3.7 through 11.3.10 two more times.

11.3.12 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.3.13 Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.3.14 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the volume of sample used on the benchsheet.

11.3.15 Remove the glass funnel from the top of the concentrator tube.

11.3.16 Proceed to section 11.8.

11.4 Solid Sample Screening and Assignment of Sample Preparation Protocols

11.4.1 Tare a 40 mL VOA vial

11.4.2 Add a 1 +/- 0.1 g sub-sample in accordance with KNOX-QA-0006.

11.4.3 Add 1.0 mL of 8082 surrogate mix.

11.4.4 Add 9 mL of hexane.

11.4.5 Cap tightly, and secure on a platform shaker table.

11.4.6 Shake for 1 hour, minimum.

11.4.7 Filter, using a small funnel fitted with a GF filter paper and a small amount of Sodium Sulfate into a 12ml vial marked at 10.0 ml.

11.4.8 If extract is colored in any way, transfer approximately 4ml into a fresh 12ml vial, add approximately 4ml of Sulfuric Acid, cap tightly, and shake the vial for 30 seconds.

11.4.9 Mark the vial with the work-order ID followed by "AW" and deliver both extracts to the GC analyst.

11.4.10 Perform a calibration check on the screening instrument. If the %D for both Aroclors and Surrogates is within +/-30 percent from the initial calibration, analyze the sample extracts within 12 hours of the calibration check.

11.4.11 If no pattern and no prominent peaks are present at the 1.0 ppb reporting limit, process the sample using Protocol 1.

11.4.12 If an Aroclor-like pattern is observed, calculate the estimated concentration of the largest peak expected in the determinative analysis, and assign a protocol. Use the spreadsheet named "PCB Protocol Selection" found at knxsvr1\msoffice\templates, to perform the following steps:

11.4.12.1 Calculate the concentration of the most prominent technical mixture, by comparison to Aroclor standards. (Enter the Aroclor sample concentration on the spreadsheet, in ppb). Circle the amount entered on the GC hardcopy result.

11.4.12.2 Correct the concentration for surrogate recovery. (Enter the average, or selected recovery in the spreadsheet.)

11.4.12.3 Multiply the concentration by 0.1 (the spreadsheet default) to correct for the weight percent of the largest single congener in an Aroclor mix. (This is done by the spreadsheet.) This value may be changed to represent special cases, such as altered patterns, or unusual technical mixtures, but documentation of the rationale must accompany the spreadsheet.

11.4.12.4 Multiply the concentration by 4 to account for single-peak coelutions. (This is done by the spreadsheet).

11.4.12.5 The resulting concentration is used as the estimate for the largest peak expected in the determinative analysis. Assign the protocol for each sample according to Table 12.

11.4.12.6 Have an independent analyst review the data entry, and protocol assignments, initial and date the spreadsheet. Attach the spreadsheet and supporting GC data to the bench worksheets.

11.4.12.7 Adjust the sample volume, spiking volume, split ratio, final volume value, and bench dilution to reflect the selected protocol.

11.5 Solid Sample Extraction (samples containing more than 1% solids.)

11.5.1 Sample Pretreatment

11.5.1.1 Tissue Samples – This section uses protocol 1 as an example. If another protocol has been assigned, the sample amount extracted, spike volumes and percent of extract used is modified based on section 11.4.12

11.5.1.1.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is blended to provide a homogeneous sample.

11.5.1.1.2 Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender.

11.5.1.1.3 Weigh out 10 grams of the homogenized tissue sample. Add the 10 g sample along with 20 g of sodium sulfate to a laboratory blender. Blend the

tissue/sodium sulfate mixture, while adding dry ice as necessary, to achieve a powder like consistency.

11.5.1.1.4 Record the sample and weight on the sample prep sheet.

11.6 Soxhlet Extraction This section uses protocol 1 as an example. If another protocol has been assigned, the sample amount extracted, spike volumes and percent of extract used is modified based on section 11.4.12

11.6.1.1 Prepare and label the required number of Soxhlet systems.

11.6.1.1.1 The Soxhlet is prepared by cleaning and rinsing per section 5, adding an extraction thimble and glass wool plug to the Soxhlet body, charging the boiling flask with solvent, assembling the components, and precleaning by reflux for 4 hours before use.

11.6.1.2 Transfer a well-mixed 10 g aliquot of the solid sample, or the entire pretreated sample into a glass microfiber extraction thimble (+/- 0.05 grams). If specified in client requirements or a quality assurance summary by the project manager, adjust the amount weighed to achieve 10 g dry weight. Record the sample and weight on the sample prep sheet. If the entire sample is to be analyzed (XAD, filters, etc.), transfer the entire sample to the Soxhlet extractor. If an extraction thimble is not being used, sandwich the sample between glass wool plugs in the extractor. Small portions of acetone may be used to aid in the transfer of XAD. If necessary, weigh the XAD sampling tube both before and after the XAD is removed and record the weights.

11.6.1.3 Sand, baked at 450° C, is used for the blank and OPR. Transfer 10g of sand into an extraction thimble. Record the sample weight on the sample prep sheet.

11.6.1.3.1 If the matrix is tissue samples, sodium sulfate and corn oil or vegetable oil or fish oil) is used for the blank and OPR. Transfer 20 grams of the sodium sulfate and several small chips of dry ice into an extraction thimble. Record the sample weight on the sample prep sheet.

11.6.1.4 Spike each sample with 1 mL of the internal standard solution (see section 7.12.8) and add a small amount of glass wool to the top of the extraction thimble.

11.6.1.4.1 Spike the OPR with 1 mL of the native spiking solutions (see section 7.12.7) prior to adding the glass wool.

11.6.1.5 Pour approximately 350 mL of the extraction solvent into a 500 mL round bottom flask. Place the flask in the heating mantle. Add about 10-15 boiling beads and several Teflon™ boiling chips.

Note: Hexane/Acetone is the preferred solvent to be used for extraction but in certain cases (i.e. XAD extraction) MeCl2/Acetone may be a better choice.

11.6.1.6 Place the extraction thimble in the glass Soxhlet extractor.

11.6.1.7 Assemble the Soxhlet system and secure to the lab supports.

11.6.1.8 Adjust the temperature of the heating mantle to bring the solvent in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour.

11.6.1.9 Soxhlet extract the sample in the above manner for 16 hours.

11.6.1.10 Turn off the heating mantle and allow the Soxhlet apparatus to cool.

11.6.1.11 Remove the condensers and allow the Soxhlet extractor chamber to empty, then remove the Soxhlet extractor from the 500 mL round bottom flask.

11.6.1.12 Place a 3-ball Snyder column on the 500 mL round bottom flask. Pre-wet the Snyder column with 1 mL of hexane and concentrate the extract to approximately 10 mL

11.6.1.13 Transfer the extract into a 40 mL vial, rinsing the 500 mL flask or concentrator tube 3 times with 3 mL of MeCl2/Acetone or Hexane/Acetone. Add the rinsings to the 40 mL vial.

11.6.1.14 Place the 40 mL vials into the N-EVAP concentration device and reduce the volume to approximately 0.5 mL. Do not allow the sample to go to dryness at any time. Add 5 mL of hexane and swirl the vial. Reduce the volume of hexane to approximately 0.5 mL again to complete the solvent exchange. Adjust the final volume of the extract with hexane to 15 mL for acid cleanup or 2 mL for column cleanup. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipette to the vial to aid in dissolving the sample. Proceed to section 11.9.

11.7 Waste Sample Extraction

11.7.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.7.2 Add an appropriate amount of sample (e.g. 1.0g) to a 40 mL VOA vial. Spike the sample with 1 mL of the internal standard spiking solution (see section 7.12.8). Record the spike solution number and the volume spiked. Add hexane to bring the volume to 15 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipette to the vial to aid in dissolving the sample. Proceed to section 11.9.

11.7.3 Record the weights and volumes used on the laboratory bench sheets.

11.8 Macro Extract Concentration by Rapid-Vap

11.8.1 Preheat the unit to the appropriate temperature for the solvent used in the extraction.

11.8.2 Set the operating parameters on the programmer. For example, if there is 300 ml of a methylene chloride extract, the following parameters may be used and should be adjusted as needed:

| | |
|---|---|
| Temperature | 30 °C |
| Vortex Speed | 30%, to be increased at a later time |
| Nitrogen | 7-9 psi |
| Timer Set | 30 minutes |

11.8.3 Place 600 ml concentrator tubes containing the extract in the Rapid-Vap. Begin concentrating the extract, adjust the vortex speed for the proper rate of concentration.

11.8.4 When the extract has been concentrated to less than 20 mL, add approximately 60 mL of hexane. Concentrate the extract to a final volume of approximately 2 ml. Shut off the nitrogen flow and turn off the Rapid-Vap or remove the 600 mL concentrator tube to prevent further concentration.

11.8.5 Transfer the extract to a 40 ml vial with a 9" disposable pipet, rinsing the sample tube three times with 3 ml of hexane. Reduce the volume in the 40 mL vial using the N-Evap to approximately 2 ml and proceed to extract cleanup in section 11.9. If no additional cleanups are to be performed continue with the following steps to dry the extract.

11.8.6 Prepare a small funnel by putting a small plug of pre-cleaned glass wool to the bottom of the funnel and adding a layer of sodium sulfate on top of the glass wool.

11.8.7 Pipet the extract from the Rapi-Vap concentrator tube and through the funnel containing the sodium sulfate into a 40ml vial.

11.8.8 Rinse the concentrator tube 3 times with approximately 3ml of hexane for each rinse. The sodium sulfate funnel then should be rinsed with an additional 2ml of hexane. Proceed to micro concentration in section 11.9.4.10.

11.9 Extract Cleanup

11.9.1 If the sample is to be analyzed for PCB's only, use the entire extract for the cleanup procedures. If additional analyses (example: Dioxins, Pesticides, PAH's, or Semi-volatiles) are to be performed on the extract, split the extract in equal portions for each analysis. Label each split portion with the sample ID and the analysis. Proceed with cleanup on the portion labeled for PCB analysis.

11.9.2 Spike each sample extract with 1 mL of the cleanup standard solution (see section 7.12.9).

11.9.3 Acid Cleanup

11.9.3.1 The acid cleanup is employed when sample extracts are colored and/or oily in

appearance.

11.9.3.2 Slowly add 15 mL of concentrated sulfuric acid to the 15 mL extract in the 40 mL vial and shake for 2 minutes. If an emulsion forms, discontinue shaking. Vent the vial frequently while shaking. Let the vial stand for a minimum of 10 minutes and remove the aqueous layer with a glass pipette. Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.9.3.3 Add 15 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 2 minutes. Vent the vial frequently while shaking. Let the vial stand for 10 minutes and remove the aqueous layer with a glass pipet. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.9.3.4 Reduce the extract volume to approximately 2 ml.

11.9.3.5 Proceed to Florisil® cleanup.

11.9.4 Florisil® Column Cleanup

11.9.4.1 Place a small ball of glass wool in the bottom of a glass chromatography column.

11.9.4.2 Attach the column to the lab support in the hood.

11.9.4.3 Pack the Florisil® column with the following layers. Add the column packing while tapping the column to settle the contents to prevent channeling. The order of the layers is from bottom to top.

11.9.4.3.1 Layer 1 - 8 cm (15 g) of Florisil®.

11.9.4.3.2 Layer 2 - 2 cm (2 g) of sodium sulfate.

11.9.4.4 Place a Rapid-Vap concentrator tube under each column to catch the solvents as they filter through the column.

11.9.4.5 Pour 70 mL of 6% diethyl ether in hexane (v/v) into a graduate cylinder and save for later use in the procedure (one graduate cylinder for each column).

11.9.4.6 Wet the column with hexane to remove any air bubbles and discard this hexane into the solvent waste. Take care not to let the column drip dry at any time during this procedure.

11.9.4.7 Just before the level of hexane reaches the top of the sodium sulfate layer, transfer the sample extract into the top of the column. Rinse the vial 3 times with 2 mL portions of hexane and add these rinsings to the column.

11.9.4.8 Just before the sample volume reaches the top of the sodium sulfate, pour the 200 mL of 6% diethyl ether in hexane (v/v) into the top of the column and allow this to drip through the column and into the concentrator tube.

11.9.4.9 Reduce the volume as described in section 11.8. Place the concentrator tube or 40 mL vial containing the extract in the N-EVAP concentration apparatus and reduce the solvent volume to approximately 0.3 ml.

11.9.4.10 Transfer the concentrated extract into a 1.1 mL tapered mini-vial, rinsing 2 times with small amounts of hexane. Label the mini vial with the sample ID.

11.9.4.11 For aqueous samples, add 20 µL of the recovery standard solution (see section 7.12.11) to the mini-vial before transferring the extract into the minivial. Then reduce the extract volume back down to 20 µL. Take the mini-vial to the GC/MS lab for analysis.

11.9.4.12 For all other samples, add 100 µL of the recovery standard solution (see section 7.12.11) to the mini-vial before transferring the extract into the minivial. Then reduce the extract volume back down to 100 µL. If the extract has been split for other analyses, adjust the final volumes and recovery standard amounts by the split factor to achieve a comparable analysis sensitivity (example: Extract split in half for PCB and Dioxin analysis, use 50 µL of recovery standard solution and concentrate to a final volume of 50 µL).

11.9.4.12.1 If the sample has had a protocol other than protocol 1 assigned, dilute the extract with nonane to achieve the dilution factor shown in Table 12. Take the mini-vial to the GC/MS lab for analysis.

11.9.5 Sulfur clean-up by Tetrabutylammonium (TBA)

11.9.5.1 Bring the sample extract to between 5 ml and 10 ml in a 40 ml vial. Caution: Do not let the extract volume drop below 1 ml, as loss of analytes may occur.

11.9.5.2 Add 1.0 ml of TBA sulfite reagent and 2.0 ml of 2-propanol to the vial containing the extract. Shake the vial vigorously for 1 minute.

11.9.5.3 If the extract is colorless or the initial color is unchanged and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more sodium sulfite in approximately 0.10 g portions until a solid residue remains after repeated shaking.

11.9.5.4 Add 5ml of reagent water and shake the vial for 1 minute. Allow the layers to separate (at least 5 minutes). Filter the hexane layer (the top layer) through a small funnel filled with sodium sulfate that has been pre-wetted with hexane and into a clean 40 ml vial.

11.9.5.5 Add 2 ml of fresh hexane to the clean-up vial. Shake for 30 seconds and allow the layers to separate again. Filter the hexane portion through the sodium sulfate funnel and into the clean 40ml vial.

11.9.5.6 Repeat step 11.9.5.5 once.

11.9.5.7 Rinse the sodium sulfate funnel with 2ml of hexane.

11.9.5.8 Proceed to section 11.9.4.10 for final concentration and transfer to a mini-vial

11.10 Sample Analysis

11.10.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data beginning at 8 minutes and ending after decachlorobiphenyl has eluted from the column.

11.10.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename
Analyst
Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.10.3 Generate integrated ion chromatograms for the masses listed in Table 8 that encompass the expected retention windows of the PCB homologous series.

11.10.4 Generate a reduced peak list file from the integrations show in the ion chromatograms.

11.10.5 Load the reduced peak list file into the calculation software.

11.10.6 The RTs of the unambiguous labeled congeners (RT Markers) are used to calculate a least squares best fit regression for retention times compared to those of the retention time calibration.

11.10.7 The resulting regression is used to calculate predicted retention times for target analytes. These predicted retention times are used by the software to identify candidate peaks for targets.

11.10.8 The analyst reviews the peaks identified as targets, and determines whether to accept the identification. This determination is made by evaluating the delta values, (RT shift from predicted), knowledge of peak patterns and observations of localized shifting.

11.10.9 An RRT window is calculated by multiplying the RRT Limit High and the RRT Limit Low by the retention time of the designated RT reference. The software applies a qualitative flag to each peak identified as a target that has a RRT outside the RRT window.

## 12 Data Analysis and Calculations

12.1 Qualitative identification criteria for PCBs.

For a gas chromatographic peak to be identified as a PCB, it must meet all of the following criteria:

12.1.1 The signals for the two exact m/z's in Table 8 must be present and must maximize within ±2 seconds.

12.1.2 The signal to noise ratio (S/N) for each GC peak at each exact m/z must be greater than or equal to (≥) 2.5. (This requirement does not apply to the secondary ion for dichlorinated biphenyls [m/z 223.9974]. High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.)

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 8 must be within the limits in Table 9. Alternately, the ratios may be within ±15% of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

12.1.4 The relative retention time of the peak for a CB must be within the RRT QC limits calculated in section 10.2.5.

Note: For native CBs determined by internal standard quantitation, a given CB congener may fall within more than one RT window and be misidentified unless the RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. Retention time regression analysis may be employed for this purpose.

12.1.5 If identification is ambiguous, (i.e. some, but not all of the identification criteria are met for a congener) an experienced analyst must determine the presence or absence of the congener.

12.2 Quantitation for PCB's.

12.2.1 Calculate the Internal Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$Ris = \frac{Ais \times Qrs}{Ars \times RRFis \times Qis} \times 100\%$$

where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

Note: In some situations, such as source testing, the extract is split for multiple

analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = Qrss \times Split$$

where:

Qrs = ng of recovery standard added to extract
Qrss = ng of recovery standard added to the split portion of the extract
Split = split ratio of the extract

12.2.2 Calculate the concentration of individual PCBs according to the following equation:

$$Concentration = \frac{As \times Qis}{Ais \times RRF \times W \times S}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)
S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis)

12.2.3 If reporting results for Total Homolog Groups, calculate the total concentration of all isomers within each homolog group by summing the concentrations of the individual PCB isomers within that homolog group.

12.2.4 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRF \times W \times S}$$

where:

N = sum of peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = sum of peak heights of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)
S = decimal expression of solids (optional, if results are requested to be

reported on dry weight basis. Note: do not use if results are to be reported by QuantIMS since it performs all necessary moisture corrections.)

12.2.5 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.1, calculate an Estimated Maximum Possible Concentration (EMPC). Use the equation in section 12.2.2, except that As should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.2.6 If the concentration in the final extract of any PCB isomer exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 1/10 may be performed on the extract. If compound concentrations exceeding the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed. The lab may report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Consultation with the client should occur before compounds are reported which exceed the calibration range.

12.3 The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. The EML's for different matrices and extract volumes are listed in Table 4. Deviations from the extraction amounts or final volumes listed will result in corresponding changes in the actual sample ML.

12.4 Flag all compound results in the sample which are below the estimated minimum level with a "J" qualifier.

12.5 Flag all compound results in the sample which were detected in the method blank with a "B" qualifier.

12.6 Flag all compound results in the sample which are above the upper calibration limit with an "E" qualifier.

12.7 Flag all compound results in the sample which are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.8 Flag compound results in the sample that may contain co-eluting compounds with a "C" qualifier.

12.8.1 Flag congeners known to coelute with a higher numbered congener with a "C" qualifier.

12.8.2 Flag congeners that coelute with a lower numbered congener with a "Cx" qualifier where x is the CAS PCB number of the lowest numbered congener in the coeluting group.

12.9 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier.

12.10 Data review

12.10.1 Refer to Figure 3 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.10.2 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.10.3 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.10.4 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.10.5 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.10.6 All items listed on the data review checklist must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. An example data review checklist is shown in Figure 3.

## 13 Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP S-Q-003 current revision based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in STL Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

## 14 Pollution Prevention

14.1 All attempts will be made to minimize the use of solvents and standard materials.

## 15 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Waste methylene chloride from sample preparation, glassware rinsing and sodium sulfate pre-rinsing shall be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.
- Waste acetone and hexane from glassware and acid rinsing shall be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container.
- Extracted PUF filters, XAD-2 resin, paper funnel filters, glass wool, fish/crawfish and soil contaminated with methylene chloride shall be placed in the flammable waste stream, contained in a steel or poly satellite accumulation container.
- Contaminated sulfuric acid used during extract cleanup shall be placed in the acidic waste stream, contained in a poly satellite accumulation container.
- Extracted aqueous samples, contaminated with methylene chloride shall be placed in the organic water waste stream, contained in a poly satellite accumulation container.

## 16 References

16.1 STL Quality Management Plan (current revision).

16.2 STL Knoxville Laboratory Quality Manual (LQM), current revision.

16.3 USEPA SW-846 "Test Methods for Evaluating Solid Waste" Third Edition.

16.4 Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution

HRGC/HRMS [Revision B], EPA#: 821/B-94-005a YEAR: 1994

16.5 Method 1668: Toxic Polychlorinated Biphenyls by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry [Draft], EPA#: 821/R-97-001 YEAR: 1997.

16.6 Ballschmiter, K. and M. Zell, "Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography", *Fresenius Z. Anal. Chem.*, 302:20-31 (1980).

16.7 Schulte, E. and R. Malisch, "Berechnung der Wahren PCB-Gehalte in Umweltproben I. Ermittlung der Zusammensetzung Zweier Technischer PCB-Gemische," *Fresenius Z. Anal. Chem.*, 314:545-551 (1983).

16.8 Guitart, R., P. Puig and J. Gómez-Catalán, "Requirement for a Standardized Nomenclature Criterion for PCBs: Computer-Assisted Assignment of Correct Congener Denomination and Numbering," *Chemosphere*, 27(8):1451-1459 (1993).

16.9 Rigaudy, J. and Klesney, S.P., Nomenclature of Organic Chemistry, Pergamon, 1979.

16.10 Pretsch, Clerc, Seibl, Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Second Edition, Springer-Verlag, 1989.

16.11 CRC Handbook of Chemistry and Physics, 71st edition, CRC Press, 1990-1991.

## 17 Miscellaneous

17.1 Deviations from EPA Method 1668, Revision A.

17.1.1 Additional recovery standards are used in this procedure. The additional standards are listed in Table 1.

17.1.2 Additional labeled standards are used in this procedure as field sampling surrogates. The additional standards are listed in Table 1.

17.1.3 A solvent mixture of acetone: hexane (1:1 volume) is used instead of toluene for extractions of solids and samples containing particles.

17.1.4 Fish oil is allowed as an alternative to corn oil or other vegetable oil as a reference matrix for tissues.

17.1.5 The method authors had observed that when their columns were degraded, PCBs 156 and 157 became resolved. The method indicates that the compounds must coelute within 2 seconds. Using constant flow conditions, this laboratory has resolved PCB 156 from PCB 157 on columns that are not degraded. This procedure does not require the coelution of the two isomers, but requires that the retention times may not change significantly in relative retention times, in accordance with section 10.4.5.6.

17.1.6 The calibration procedure in the method calls for a single point standard for the non-Toxic/LOC congeners. This procedure uses a multi-point calibration for all 209

congeners.

17.1.7 This procedure uses MID groups that differ from the method. The procedure uses 4 groups, rather than 6, to improve instrument stability, by holding the magnet current steady for longer periods. Therefore alternate PFK lock masses are monitored, to reflect the mass ranges of the procedure's MID groups.

17.1.8 This procedure uses average retention times (and average relative retention times) produced by triplicate analyses of the 5 mixes specified, rather than single analyses of the diluted 209 standard.

17.1.9 The retention times in Table 2 do not match those provided in the method. The chromatographic conditions have been changed to improve chromatographic resolution. The procedure requires the minimum elution time of 55 minutes for PCB 209.

17.1.10 The calibration verification procedures in the method call for updating the retention times, relative retention times and response factors for non-Toxic compounds during daily calibration and use the retention times, relative retention times and response factors from the initial calibration for Toxic and LOC compounds. This laboratory uses the retention times and relative retention times from triplicate analyses of the 5-mix series, which contains all congeners, and uses response factors from the initial calibration for all 209 compounds. The practice of updating the relative retention times of only a subset of compounds causes significant error in the linear regression prediction formulas used by targeting software to identify the compounds. This procedure has provisions for updating all RT's and RRT's by analyzing a new retention time calibration series.

17.1.11 The EMLs listed in Table 4 differ from those listed in the reference method. The EMLs are set above the mean plus 2 standard deviations for the higher of detections or EDLs for method blanks. In no case is the EML lower than the low calibration limit. The survey period was approximately 14 months.

17.2 Summary of modifications to SOP from Revision 3.

17.2.1 Quantitation references were changed for PCB 52L, PCB 155L, PCB 189L and PCB 202L to PCB 32L, PCB 101L, PCB194L and PCB 180L, respectively.

17.3 Summary of modifications to SOP from Revision 2.

17.3.1 Added section 2.1, indicating the use of sample screening. Removed reference to 10g sample size in section 2.2.

17.3.2 Added sections 3.4, 3.6, 3.14, 3.20, and 3.26.

17.3.3 Added subsections to section 6.8.1, specifying GPC apparatus components.

17.3.4 Removed requirement to bake sodium sulfate. Performance is better with methylene chloride rinse.

17.3.5 Changed storage temperature for Florisil® to 125-135 °C.

17.3.6 Modified section 7.12.5.3, changed concentration to 1000 ng/mL

17.3.7 Inserted 3 notes, in sections 7.12.7, 7.12.8 and 7.12.9 describing the high and low concentration spiking solutions used, depending on final volume targeted.

17.3.8 Modified section 7.12.11, added dual final volume information.

17.3.9 Modified section 9.4 to include corn oil or fish oil as the reference matrix for tissue samples.

17.3.10 Modified section 9.4 to include consultation with the Project Manager for method blank detections above the EML.

17.3.11 Re-ordered subsections and modified section 10.

17.3.12 Struck language from section 10.2.5.1.1 and 10.2.5.1.2 making exceptions for electronic pressure control.

17.3.13 Added triplicate analysis of 5 congener mixes for retention time assignment. (Section 10.2.3).

17.3.14 Added multi-point calibration of all 209 congeners.

17.3.15 Modified section 10.3.2 and added section 10.3.2.1 to describe performing mass resolution and mass accuracy checks on masses throughout the MID groups. Added section 10.3.3 which allows for resolving power of 8,000 at MID extremes (per 1668A).

17.3.16 Added section 10.2 describing retention time calibration.

17.3.17 Removed comment from section 10.4.5.7 excepting RT and RRT limits for GCs with electronic pressure control.

17.3.18 Added section 11.4 and subsections, describing the procedure for screening and assigning sample preparation protocols.

17.3.19 Modified section 11.6.1.3.1 to add corn, vegetable or fish oil to the blank and OPR samples.

17.3.20 Added section 11.9.4.11, describing the micro-concentration of aqueous samples to 20 µL.

17.3.21 Added section 11.9.4.12 and subsection, describing the dilution of extracts according to the assigned protocol.

17.3.22 Added section 13.2, describing the requirement for MDL studies.

17.3.23 Added Table 12 - Assignment of Sample Preparation Protocols

17.3.24 Table 1 - Deleted 3L6, Added 1L, 4L, 9L, 19L, 54L, 79L, 104L, 127L, 155L, 188L, and 205L. Added CAS Registry Numbers. Changed usage on several labeled standards.

17.3.25 Table 2 – Replaced with values from 1668A. Added additional recovery standards and sampling surrogates. Calculated new RRT & limits where applicable.

17.3.26 Revised values in Table 3 to reflect new minimum calibration level, CS-0.5. Dropped the high level standard for sampling surrogates. Added LCLs for biological tissues. Added footnote describing application of multipliers for additional preparation protocols.

17.3.27 Replaced Table 4 to reflect updated estimated minimum levels. Added EMLs for biological tissues. Added footnote describing application of multipliers for additional preparation protocols.

17.3.28 – Added additional analytes and labeled standards. Added concentrations for 20µL extracts.

17.3.29 Table 6 – Added additional analytes and labeled standards. Changed CS0.2 to CS0.5. Added footnote identifying level 3 as the calibration verification level.

17.3.30 Table 8 - Changed monitored masses for nona and deca. Added 13C-Tetra ions to MID group 1. Changed MID 1 QC mass from 268.9824 to 280.9824. Changed MID 2 QC mass from 342.9792 to 380.97605.

17.3.31 Table 9 - Replaced calculated ratios and limits with 1668A ratios and limits.

17.3.32 Table 10 – Added additional analytes and labeled standards. Expressed limits in percent instead of concentration.

17.4 List of tables and figures referenced in the body of the SOP.

17.4.1 Table 1 - Polychlorinated Biphenyls Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

17.4.2 Table 2 - RT References, Quantitation References, Retention Times (RT), and Relative Retention Times (RRTs) for the 209 CB congeners on SPB-Octyl

17.4.3 Table 3– Low Calibration Levels Based on Various Final Extract Volumes

17.4.4 Table 4 - Estimated Minimum Levels – Matrix and Concentration

17.4.5 -Concentration of Stock & Spiking Solutions Containing PCBs & Labeled Compounds

17.4.6 Table 6 - Concentration of PCBs in Calibration Solutions

17.4.7 Table 7 - Window Defining Mixture and SPB-Octyl Resolution Test Compounds

17.4.17 History of Revisions

| REV NO. | DATE | PAGES AFFECTED | REASON FOR REVISION |
|---|---|---|---|
| 0 | 09/28/99 | All | Initial Revision of Method |
| 1 | 10/12/01 | See KNOX-ID-0013-R1 | Updated based on EPA1668A |
| 2 | 01/17/02 | See KNOX-ID-0013-R2 | Updated based on EPA1668A |
| 3 | 08/17/05 | See Section 17.3 | Updated based on EPA1668A |

# Table 1

## Polychlorinated Biphenyls Determined by HRGC/HRMS

| BZ/IUPAC Number[1] | PCB Chemical Structure Name[2] | CAS Registry[3] Number | Labeled Analog | CAS Registry[3] | Usage |
|---|---|---|---|---|---|
| 1 | 2-monochlorobiphenyl | 2051-60-7 | $^{13}C_{12}$-2-monochlorobiphenyl | 234432-85-0 | Internal Std |
| 2 | 3-monochlorobiphenyl | 2051-61-8 | | | |
| 3 | 4-monochlorobiphenyl | 2051-62-9 | $^{13}C_{12}$-4-monochlorobiphenyl | 208263-77-8 | Internal Std |
| 4 | 2,2'-dichlorobiphenyl | 13029-08-8 | $^{13}C_{12}$-2,2'-dichlorobiphenyl | 234432-86-1 | Internal Std |
| 5 | 2,3-dichlorobiphenyl | 16605-91-7 | | | |
| 6 | 2,3'-dichlorobiphenyl | 25569-80-6 | | | |
| 7 | 2,4-dichlorobiphenyl | 33284-50-3 | | | |
| 8 | 2,4'-dichlorobiphenyl | 34883-43-7 | $^{13}C_{12}$-2,4'-dichlorobiphenyl | | Surrogate Std |
| 9 | 2,5-dichlorobiphenyl | 34883-39-1 | $^{13}C_{12}$-2,5-dichlorobiphenyl | 250694-89-4 | Recovery Std |
| 10 | 2,6-dichlorobiphenyl | 33146-45-1 | | | |
| 11 | 3,3'-dichlorobiphenyl | 2050-67-1 | | | |
| 12 | 3,4-dichlorobiphenyl | 2974-92-7 | | | |
| 13 | 3,4'-dichlorobiphenyl | 2974-90-5 | | | |
| 14 | 3,5-dichlorobiphenyl | 34883-41-5 | | | |
| 15 | 4,4'-dichlorobiphenyl | 2050-68-2 | $^{13}C_{12}$-4,4'-dichlorobiphenyl | 208263-67-6 | Internal Std |
| 16 | 2,2',3-trichlorobiphenyl | 38444-78-9 | | | |
| 17 | 2,2',4-trichlorobiphenyl | 37680-66-3 | | | |
| 18 | 2,2',5-trichlorobiphenyl | 37680-65-2 | | | |
| 19 | 2,2',6-trichlorobiphenyl | 38444-73-4 | $^{13}C_{12}$-2,2',6-trichlorobiphenyl | 234432-87-2 | Internal Std |
| 20 | 2,3,3'-trichlorobiphenyl | 38444-84-7 | | | |
| 21 | 2,3,4-trichlorobiphenyl | 55702-46-0 | | | |
| 22 | 2,3,4'-trichlorobiphenyl | 38444-85-8 | | | |
| 23 | 2,3,5-trichlorobiphenyl | 55720-44-0 | | | |
| 24 | 2,3,6-trichlorobiphenyl | 55702-45-9 | | | |
| 25 | 2,3',4-trichlorobiphenyl | 55712-37-3 | | | |
| 26 | 2,3',5-trichlorobiphenyl | 38444-81-4 | | | |
| 27 | 2,3',6-trichlorobiphenyl | 38444-76-7 | | | |
| 28 | 2,4,4'-trichlorobiphenyl | 7012-37-5 | $^{13}C_{12}$-2,4,4'-trichlorobiphenyl | 208263-76-7 | Cleanup Std |
| 29 | 2,4,5-trichlorobiphenyl | 15862-07-4 | | | |
| 30 | 2,4,6-trichlorobiphenyl | 35693-92-6 | | | |
| 31 | 2,4',5-trichlorobiphenyl | 16606-02-3 | $^{13}C_{12}$-2,4',5-trichlorobiphenyl | | Recovery Std |
| 32 | 2,4',6-trichlorobiphenyl | 38444-77-8 | $^{13}C_{12}$-2,4',6-trichlorobiphenyl | | Recovery Std |
| 33 | 2',3,4-trichlorobiphenyl (2,3',4'-trichlorobiphenyl) | 38444-86-9 | | | |
| 34 | 2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl) | 37680-68-5 | | | |
| 35 | 3,3',4-trichlorobiphenyl | 37680-69-6 | | | |
| 36 | 3,3',5-trichlorobiphenyl | 38444-87-0 | | | |
| 37 | 3,4,4'-trichlorobiphenyl | 38444-90-5 | $^{13}C_{12}$-3,4,4'-trichlorobiphenyl | 208263-79-0 | Internal Std |
| 38 | 3,4,5-trichlorobiphenyl | 53555-66-1 | | | |
| 39 | 3,4',5-trichlorobiphenyl | 38444-88-1 | | | |
| 40 | 2,2',3,3'-tetrachlorobiphenyl | 38444-93-8 | | | |
| 41 | 2,2',3,4-tetrachlorobiphenyl | 52663-59-9 | | | |
| 42 | 2,2',3,4'-tetrachlorobiphenyl | 36559-22-5 | | | |
| 43 | 2,2',3,5-tetrachlorobiphenyl | 70362-46-8 | | | |
| 44 | 2,2',3,5'-tetrachlorobiphenyl | 41464-39-5 | | | |
| 45 | 2,2',3,6-tetrachlorobiphenyl | 70362-45-7 | | | |
| 46 | 2,2',3,6'-tetrachlorobiphenyl | 41464-47-5 | | | |
| 47 | 2,2',4,4'-tetrachlorobiphenyl | 2437-79-8 | | | |
| 48 | 2,2',4,5-tetrachlorobiphenyl | 70362-47-9 | | | |
| 49 | 2,2',4,5'-tetrachlorobiphenyl | 41464-40-8 | | | |
| 50 | 2,2',4,6-tetrachlorobiphenyl | 62796-65-0 | | | |
| 51 | 2,2',4,6'-tetrachlorobiphenyl | 68194-04-7 | | | |
| 52 | 2,2',5,5'-tetrachlorobiphenyl | 35693-99-3 | $^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl | 160901-66-6 | Recovery Std |
| 53 | 2,2',5,6'-tetrachlorobiphenyl | 41464-41-9 | | | |
| 54 | 2,2',6,6'-tetrachlorobiphenyl | 15968-05-5 | $^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl | 234432-88-3 | Internal Std |
| 55 | 2,3,3',4-tetrachlorobiphenyl | 74338-24-2 | | | |
| 56 | 2,3,3',4'-tetrachlorobiphenyl | 41464-43-1 | | | |

| BZ/IUPAC Number[1]. | PCB Chemical Structure Name[2] | CAS Registry[3] Number | Labeled Analog | CAS Registry[3] | Usage |
|---|---|---|---|---|---|
| 57 | 2,3,3',5-tetrachlorobiphenyl | 70424-67-8 | | | |
| 58 | 2,3,3',5'-tetrachlorobiphenyl | 41464-49-7 | | | |
| 59 | 2,3,3',6-tetrachlorobiphenyl | 74472-33-6 | | | |
| 60 | 2,3,4,4'-tetrachlorobiphenyl | 33025-41-1 | | | |
| 61 | 2,3,4,5-tetrachlorobiphenyl | 33284-53-6 | | | |
| 62 | 2,3,4,6-tetrachlorobiphenyl | 54230-22-7 | | | |
| 63 | 2,3,4',5-tetrachlorobiphenyl | 74472-34-7 | | | |
| 64 | 2,3,4',6-tetrachlorobiphenyl | 52663-58-8 | | | |
| 65 | 2,3,5,6-tetrachlorobiphenyl | 33284-54-7 | | | |
| 66 | 2,3',4,4'-tetrachlorobiphenyl | 32598-10-0 | | | |
| 67 | 2,3',4,5-tetrachlorobiphenyl | 73575-53-8 | | | |
| 68 | 2,3',4,5'-tetrachlorobiphenyl | 73575-52-7 | | | |
| 69 | 2,3',4,6-tetrachlorobiphenyl | 60233-24-1 | | | |
| 70 | 2,3',4',5-tetrachlorobiphenyl | 32598-11-1 | | | |
| 71 | 2,3',4',6-tetrachlorobiphenyl | 41464-46-4 | | | |
| 72 | 2,3',5,5'-tetrachlorobiphenyl | 41464-42-0 | | | |
| 73 | 2,3',5',6-tetrachlorobiphenyl | 74338-23-1 | | | |
| 74 | 2,4,4',5-tetrachlorobiphenyl | 32690-93-0 | | | |
| 75 | 2,4,4',6-tetrachlorobiphenyl | 32598-12-2 | | | |
| 76 | 2',3,4,5-tetrachlorobiphenyl (2,3',4',5'-tetrachlorobiphenyl) | 70362-48-0 | | | |
| 77 | 3,3',4,4'-tetrachlorobiphenyl | 32598-13-3 | $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl | 160901-67-7 | Internal Std |
| 78 | 3,3',4,5-tetrachlorobiphenyl | 70362-49-1 | | | |
| 79 | 3,3',4,5'-tetrachlorobiphenyl | 41464-48-6 | $^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl | | Surrogate Std |
| 80 | 3,3',5,5'-tetrachlorobiphenyl | 33284-52-5 | | | |
| 81 | 3,4,4',5-tetrachlorobiphenyl | 70362-50-4 | $^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl | 160901-68-8 | Internal Std |
| 82 | 2,2',3,3',4-pentachlorobiphenyl | 52663-62-4 | | | |
| 83 | 2,2',3,3',5-pentachlorobiphenyl | 60145-20-2 | | | |
| 84 | 2,2',3,3',6-pentachlorobiphenyl | 52663-60-2 | | | |
| 85 | 2,2',3,4,4'-pentachlorobiphenyl | 65510-45-4 | | | |
| 86 | 2,2',3,4,5-pentachlorobiphenyl | 55312-69-1 | | | |
| 87 | 2,2',3,4,5'-pentachlorobiphenyl | 38380-02-8 | | | |
| 88 | 2,2',3,4,6-pentachlorobiphenyl | 55215-17-3 | | | |
| 89 | 2,2',3,4,6'-pentachlorobiphenyl | 73575-57-2 | | | |
| 90 | 2,2',3,4',5-pentachlorobiphenyl | 68194-07-0 | | | |
| 91 | 2,2',3,4',6-pentachlorobiphenyl | 68194-05-8 | | | |
| 92 | 2,2',3,5,5'-pentachlorobiphenyl | 52663-61-3 | | | |
| 93 | 2,2',3,5,6-pentachlorobiphenyl | 73575-56-1 | | | |
| 94 | 2,2',3,5,6'-pentachlorobiphenyl | 73575-55-0 | | | |
| 95 | 2,2',3,5',6-pentachlorobiphenyl | 38379-99-6 | $^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl | | Surrogate Std |
| 96 | 2,2',3,6,6'-pentachlorobiphenyl | 73575-54-9 | | | |
| 97 | 2,2',3',4,5-pentachlorobiphenyl (2,2',3,4',5'-pentachlorobiphenyl) | 41464-51-1 | | | |
| 98 | 2,2',3',4,6-pentachlorobiphenyl (2,2',3,4',6'-pentachlorobiphenyl) | 60233-25-2 | | | |
| 99 | 2,2',4,4',5-pentachlorobiphenyl | 38380-01-7 | | | |
| 100 | 2,2',4,4',6-pentachlorobiphenyl | 39485-83-1 | | | |
| 101 | 2,2',4,5,5'-pentachlorobiphenyl | 37680-73-2 | $^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl | 160901-69-9 | Recovery Std |
| 102 | 2,2',4,5,6-pentachlorobiphenyl | 68194-06-9 | | | |
| 103 | 2,2',4,5',6-pentachlorobiphenyl | 60145-21-3 | | | |
| 104 | 2,2',4,6,6'-pentachlorobiphenyl | 56558-16-8 | $^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl | 234432-89-4 | Internal Std |
| 105 | 2,3,3',4,4'-pentachlorobiphenyl | 32598-14-4 | $^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl | 160901-70-2 | Internal Std |
| 106 | 2,3,3',4,5-pentachlorobiphenyl | 70424-69-0 | | | |
| 107/109 | 2,3,3',4,6-pentachlorobiphenyl | 74472-35-8 | | | |
| 108/107 | 2,3,3',4',5-pentachlorobiphenyl | 70424-68-9 | | | |
| 109/108 | 2,3,3',4,5'-pentachlorobiphenyl | 70362-41-3 | | | |
| 110 | 2,3,3',4',6-pentachlorobiphenyl | 38380-03-9 | | | |
| 111 | 2,3,3',5,5'-pentachlorobiphenyl | 39635-32-0 | $^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl | 160901-71-3 | Cleanup Std |
| 112 | 2,3,3',5,6-pentachlorobiphenyl | 74472-36-9 | | | |
| 113 | 2,3,3',5',6-pentachlorobiphenyl | 68194-10-5 | | | |
| 114 | 2,3,4,4',5-pentachlorobiphenyl | 74472-37-0 | $^{13}C_{12}$-2,3,4,4',5-pentachlorobiphenyl | 160901-72-4 | Internal Std |
| 115 | 2,3,4,4',6-pentachlorobiphenyl | 74472-38-1 | | | |

| BZ/IUPAC Number[1] | PCB Chemical Structure Name[2] | CAS Registry[3] Number | Labeled Analog | CAS Registry[3] | Usage |
|---|---|---|---|---|---|
| 116 | 2,3,4,5,6-pentachlorobiphenyl | 18259-05-7 | | | |
| 117 | 2,3,4',5,6-pentachlorobiphenyl | 68194-11-6 | | | |
| 118 | 2,3',4,4',5-pentachlorobiphenyl | 31508-00-6 | $^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl | 160901-73-5 | Internal Std |
| 119 | 2,3',4,4',6-pentachlorobiphenyl | 56558-17-9 | | | |
| 120 | 2,3',4,5,5'-pentachlorobiphenyl | 68194-12-7 | | | |
| 121 | 2,3',4,5',6-pentachlorobiphenyl | 56558-18-0 | | | |
| 122 | 2',3,3',4,5-pentachlorobiphenyl (2,3,3',4',5'-pentachlorobiphenyl) | 76842-07-4 | | | |
| 123 | 2',3,4,4',5-pentachlorobiphenyl (2,3',4,4',5'-pentachlorobiphenyl) | 65510-44-3 | $^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl | 160901-74-6 | Internal Std |
| 124 | 2',3,4,5,5'-pentachlorobiphenyl (2,3',4',5',5-pentachlorobiphenyl) | 70424-70-3 | | | |
| 125 | 2',3,4,5,6'-pentachlorobiphenyl (2,3',4',5',6-pentachlorobiphenyl) | 74472-39-2 | | | |
| 126 | 3,3',4,4',5-pentachlorobiphenyl | 57465-28-8 | $^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl | 160901-75-7 | Internal Std |
| 127 | 3,3',4,5,5'-pentachlorobiphenyl | 39635-33-1 | $^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl | | Recovery Std |
| 128 | 2,2',3,3',4,4'-hexachlorobiphenyl | 38380-07-3 | | | |
| 129 | 2,2',3,3',4,5-hexachlorobiphenyl | 55215-18-4 | | | |
| 130 | 2,2',3,3',4,5'-hexachlorobiphenyl | 52663-66-8 | | | |
| 131 | 2,2',3,3',4,6-hexachlorobiphenyl | 61798-70-7 | | | |
| 132 | 2,2',3,3',4,6'-hexachlorobiphenyl | 38380-05-1 | | | |
| 133 | 2,2',3,3',5,5'-hexachlorobiphenyl | 35694-04-3 | | | |
| 134 | 2,2',3,3',5,6-hexachlorobiphenyl | 52704-70-8 | | | |
| 135 | 2,2',3,3',5,6'-hexachlorobiphenyl | 52744-13-5 | | | |
| 136 | 2,2',3,3',6,6'-hexachlorobiphenyl | 38411-22-2 | | | |
| 137 | 2,2',3,4,4',5-hexachlorobiphenyl | 35694-06-5 | | | |
| 138 | 2,2',3,4,4',5'-hexachlorobiphenyl | 35065-28-2 | $^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl | 160901-76-8 | Recovery Std |
| 139 | 2,2',3,4,4',6-hexachlorobiphenyl | 56030-56-9 | | | |
| 140 | 2,2',3,4,4',6'-hexachlorobiphenyl | 59291-64-4 | | | |
| 141 | 2,2',3,4,5,5'-hexachlorobiphenyl | 52712-04-6 | | | |
| 142 | 2,2',3,4,5,6-hexachlorobiphenyl | 41411-61-4 | | | |
| 143 | 2,2',3,4,5,6'-hexachlorobiphenyl | 68194-15-0 | | | |
| 144 | 2,2',3,4,5',6-hexachlorobiphenyl | 68194-14-9 | | | |
| 145 | 2,2',3,4,6,6'-hexachlorobiphenyl | 74472-40-5 | | | |
| 146 | 2,2',3,4',5,5'-hexachlorobiphenyl | 51908-16-8 | | | |
| 147 | 2,2',3,4',5,6-hexachlorobiphenyl | 68194-13-8 | | | |
| 148 | 2,2',3,4',5,6'-hexachlorobiphenyl | 74472-41-6 | | | |
| 149 | 2,2',3,4',5',6-hexachlorobiphenyl | 38380-04-0 | | | |
| 150 | 2,2',3,4',6,6'-hexachlorobiphenyl | 68194-08-1 | | | |
| 151 | 2,2',3,5,5',6-hexachlorobiphenyl | 52663-63-5 | | | |
| 152 | 2,2',3,5,6,6'-hexachlorobiphenyl | 68194-09-2 | | | |
| 153 | 2,2',4,4',5,5'-hexachlorobiphenyl | 35065-27-1 | $^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl | | Surrogate Std |
| 154 | 2,2',4,4',5,6'-hexachlorobiphenyl | 60145-22-4 | | | |
| 155 | 2,2',4,4',6,6'-hexachlorobiphenyl | 33979-03-2 | $^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl | 234432-90-7 | Internal Std |
| 156 | 2,3,3',4,4',5-hexachlorobiphenyl | 38380-08-4 | $^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl | 160901-77-9 | Internal Std |
| 157 | 2,3,3',4,4',5'-hexachlorobiphenyl | 69782-90-7 | $^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl | 160901-78-0 | Internal Std |
| 158 | 2,3,3',4,4',6-hexachlorobiphenyl | 74472-42-7 | | | |
| 159 | 2,3,3',4,5,5'-hexachlorobiphenyl | 39635-35-3 | | | |
| 160 | 2,3,3',4,5,6-hexachlorobiphenyl | 41411-62-5 | | | |
| 161 | 2,3,3',4,5',6-hexachlorobiphenyl | 74472-43-8 | | | |
| 162 | 2,3,3',4',5,5'-hexachlorobiphenyl | 39635-34-2 | | | |
| 163 | 2,3,3',4',5,6-hexachlorobiphenyl | 74472-44-9 | | | |
| 164 | 2,3,3',4',5',6-hexachlorobiphenyl | 74472-45-0 | | | |
| 165 | 2,3,3',5,5',6-hexachlorobiphenyl | 74472-46-1 | | | |
| 166 | 2,3,4,4',5,6-hexachlorobiphenyl | 41411-63-6 | | | |
| 167 | 2,3',4,4',5,5'-hexachlorobiphenyl | 52663-72-6 | $^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl | 161627-18-5 | Internal Std |
| 168 | 2,3',4,4',5',6-hexachlorobiphenyl | 59291-65-5 | | | |
| 169 | 3,3',4,4',5,5'-hexachlorobiphenyl | 32774-16-6 | $^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl | 160901-79-1 | Internal Std |
| 170 | 2,2',3,3',4,4',5-heptachlorobiphenyl | 35065-30-6 | $^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl | 160901-80-4 | Internal Std |
| 171 | 2,2',3,3',4,4',6-heptachlorobiphenyl | 52663-71-5 | | | |
| 172 | 2,2',3,3',4,5,5'-heptachlorobiphenyl | 52663-74-8 | | | |
| 173 | 2,2',3,3',4,5,6-heptachlorobiphenyl | 68194-16-1 | | | |
| 174 | 2,2',3,3',4,5,6'-heptachlorobiphenyl | 38411-25-5 | | | |

| BZ/IUPAC Number[1] | PCB Chemical Structure Name[2] | CAS Registry[3] Number | Labeled Analog | CAS Registry[3] | Usage |
|---|---|---|---|---|---|
| 175 | 2,2',3,3',4,5',6-heptachlorobiphenyl | 40186-70-7 | | | |
| 176 | 2,2',3,3',4,6,6'-heptachlorobiphenyl | 52663-65-7 | | | |
| 177 | 2,2',3,3',4',5,6-heptachlorobiphenyl (2,2',3,3',4,5',6'-heptachlorobiphenyl) | 52663-70-4 | | | |
| 178 | 2,2',3,3',5,5',6-heptachlorobiphenyl | 52663-67-9 | $^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl | 160901-81-5 | Cleanup Std |
| 179 | 2,2',3,3',5,6,6'-heptachlorobiphenyl | 52663-64-6 | | | |
| 180 | 2,2',3,4,4',5,5'-heptachlorobiphenyl | 35065-29-3 | $^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl | 160901-82-6 | Recovery Std |
| 181 | 2,2',3,4,4',5,6-heptachlorobiphenyl | 74472-47-2 | | | |
| 182 | 2,2',3,4,4',5,6'-heptachlorobiphenyl | 60145-23-5 | | | |
| 183 | 2,2',3,4,4',5',6-heptachlorobiphenyl | 52663-69-1 | | | |
| 184 | 2,2',3,4,4',6,6'-heptachlorobiphenyl | 74472-48-3 | | | |
| 185 | 2,2',3,4,5,5',6-heptachlorobiphenyl | 52712-05-7 | | | |
| 186 | 2,2',3,4,5,6,6'-heptachlorobiphenyl | 74472-49-4 | | | |
| 187 | 2,2',3,4',5,5',6-heptachlorobiphenyl | 52663-68-0 | | | |
| 188 | 2,2',3,4',5,6,6'-heptachlorobiphenyl | 74487-85-7 | $^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl | 234432-91-8 | Internal Std |
| 189 | 2,3,3',4,4',5,5'-heptachlorobiphenyl | 39635-31-9 | $^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl | 160901-83-7 | Internal Std |
| 190 | 2,3,3',4,4',5,6-heptachlorobiphenyl | 41411-64-7 | | | |
| 191 | 2,3,3',4,4',5',6-heptachlorobiphenyl | 74472-50-7 | | | |
| 192 | 2,3,3',4,5,5',6-heptachlorobiphenyl | 74472-51-8 | | | |
| 193 | 2,3,3',4',5,5',6-heptachlorobiphenyl | 69782-91-8 | | | |
| 194 | 2,2',3,3',4,4',5,5'-octachlorobiphenyl | 35694-08-7 | $^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl | 208263-74-5 | Recovery Std |
| 195 | 2,2',3,3',4,4',5,6-octachlorobiphenyl | 52663-78-2 | | | |
| 196 | 2,2',3,3',4,4',5,6'-octachlorobiphenyl | 42740-50-1 | | | |
| 197 | 2,2',3,3',4,4',6,6'-octachlorobiphenyl | 33091-17-7 | | | |
| 198 | 2,2',3,3',4,5,5',6-octachlorobiphenyl | 68194-17-2 | | | |
| 199/200 | 2,2',3,3',4,5,6,6'-octachlorobiphenyl | 52663-73-7 | | | |
| 200/201 | 2,2',3,3',4,5',6,6'-octachlorobiphenyl | 40186-71-8 | | | |
| 201/199 | 2,2',3,3',4,5,5',6'-octachlorobiphenyl | 52663-75-9 | | | |
| 202 | 2,2',3,3',5,5',6,6'-octachlorobiphenyl | 2136-99-4 | $^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl | 105600-26-8 | Internal Std |
| 203 | 2,2',3,4,4',5,5',6-octachlorobiphenyl | 52663-76-0 | | | |
| 204 | 2,2',3,4,4',5,6,6'-octachlorobiphenyl | 74472-52-9 | | | |
| 205 | 2,3,3',4,4',5,5',6-octachlorobiphenyl | 74472-53-0 | $^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl | 234446-64-1 | Internal Std |
| 206 | 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl | 40186-72-9 | $^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl | 208263-75-6 | Internal Std |
| 207 | 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl | 52663-79-3 | | | |
| 208 | 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl | 52663-77-1 | $^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl | 234432-92-9 | Internal Std |
| 209 | 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl | 2051-24-3 | $^{13}C_{12}$-decachlorobiphenyl | 160901-84-8 | Internal Std |

1. The BZ number is from Ballschmiter and Zell (1980). The IUPAC number, when different from the BZ, follows the recommended changes to the BZ number per Schulte and Malisch (1983) and Guitart et al. (1993).

2. The chemical structure names are from Ballschmiter and Zell (1980). IUPAC nomenclature structure names are listed in parenthesis when different from the BZ name (source CAS Registry).

3. Chemical Abstract Service Registry number (source CAS Registry and 1668A Table 1).

Table 2

RT References, Quantitation References, Retention Times (RT), and Relative Retention Times (RRTs) for the 209 CB congeners on SPB-Octyl.

| Cl No[1] | IUPAC No[2,3] | RT Ref[4] | Quantitation Reference[5] | RT[6] | RRT[7] | RRT Limit[8] | RT Win[9] (sec) |
|---|---|---|---|---|---|---|---|
| **Monochlorobiphenyls** | | | | | | | |
| 1 | 1L | 9L | 9L | 13:08 | 0.7306 | 0.7167-0.7446 | 30 |
| 1 | 3L | 9L | 9L | 15:32 | 0.8651 | 0.8512-0.879 | 30 |
| 1 | 1 | 1L | 1L | 13:08 | 1.0008 | 0.9945-1.0072 | 10 |
| 1 | 2 | 3L | 1L/3L | 15:22 | 0.9882 | 0.985-0.9914 | 6 |
| 1 | 3 | 3L | 3L | 15:33 | 1.0011 | 0.9979-1.0043 | 6 |
| **Dichlorobiphenyls** | | | | | | | |
| 2 | 4L | 9L | 9L | 15:49 | 0.8805 | 0.8666-0.8944 | 30 |
| 2 | 9L | 9L | 9L | 17:58 | 1.0000 | 0.9884-1.0116 | 25 |
| 2 | 8L | 4L | 4L/15L | 18:52 | 1.1928 | 1.1896-1.1959 | 6 |
| 2 | 15L | 9L | 9L | 22:10 | 1.2339 | 1.2246-1.2432 | 20 |
| 2 | 4 | 4L | 4L | 15:50 | 1.0011 | 0.9958-1.0063 | 10 |
| 2 | 10 | 4L | 4L/15L | 16:02 | 1.0123 | 1.0091-1.0154 | 6 |
| 2 | 9 | 4L | 4L/15L | 18:00 | 1.1368 | 1.1337-1.14 | 6 |
| 2 | 7 | 4L | 4L/15L | 18:10 | 1.1485 | 1.1454-1.1517 | 6 |
| 2 | 6 | 4L | 4L/15L | 18:26 | 1.1646 | 1.1614-1.1677 | 6 |
| 2 | 5 | 4L | 4L/15L | 18:46 | 1.1857 | 1.1826-1.1889 | 6 |
| 2 | 8 | 4L | 4L/15L | 18:54 | 1.1937 | 1.1905-1.1968 | 6 |
| 2 | 14 | 15L | 4L/15L | 20:39 | 0.9311 | 0.9289-0.9334 | 6 |
| 2 | 11 | 15L | 4L/15L | 21:33 | 0.9715 | 0.9692-0.9737 | 6 |
| 2 | 13 | 15L | 4L/15L | 21:49 | 0.9847 | 0.9825-0.987 | 6 |
| 2 | 12 | 15L | 4L/15L | 21:54 | 0.9872 | 0.985-0.9895 | 6 |
| 2 | 15 | 15L | 15L | 22:10 | 1.0008 | 0.997-1.0045 | 10 |
| **Trichlorobiphenyls** | | | | | | | |
| 3 | 19L | 32L | 32L | 19:12 | 0.8469 | 0.8359-0.8579 | 30 |
| 3 | 32L | 32L | 32L | 22:40 | 1.0000 | 0.9978-1.0022 | 6 |
| 3 | 31L | 31L | 31L | 25:03 | 1.0000 | 0.998-1.002 | 6 |
| 3 | 28L | 31L | 31L | 25:22 | 1.0126 | 1.006-1.0193 | 20 |
| 3 | 37L | 31L | 31L | 29:32 | 1.1793 | 1.1693-1.1893 | 30 |
| 3 | 19 | 19L | 19L | 19:12 | 1.0009 | 0.9965-1.0052 | 10 |
| 3 | 30 | 19L | 19L | 21:12 | 1.1041 | 1.1015-1.1067 | 6 |
| 3 | 18 | 19L | 19L | 21:13 | 1.1054 | 1.1027-1.108 | 6 |
| 3 | 17 | 19L | 19L | 21:38 | 1.1277 | 1.1251-1.1303 | 6 |
| 3 | 27 | 19L | 19L | 21:53 | 1.1397 | 1.1371-1.1423 | 6 |
| 3 | 24 | 19L | 19L | 22:01 | 1.1473 | 1.1447-1.1499 | 6 |
| 3 | 16 | 19L | 19L | 22:08 | 1.1534 | 1.1508-1.1561 | 6 |
| 3 | 32 | 19L | 19L | 22:43 | 1.1825 | 1.1799-1.1851 | 6 |
| 3 | 34 | 19L | 37L | 24:02 | 1.2511 | 1.2485-1.2537 | 6 |
| 3 | 23 | 19L | 37L | 24:11 | 1.2599 | 1.2566-1.2618 | 6 |
| 3 | 29 | 19L | 37L | 24:32 | 1.2785 | 1.2742-1.2829 | 10 |
| 3 | 26 | 19L | 37L | 24:31 | 1.2763 | 1.2719-1.2806 | 10 |
| 3 | 25 | 37L | 37L | 24:44 | 0.8377 | 0.836-0.8394 | 6 |
| 3 | 31 | 37L | 37L | 25:05 | 0.8488 | 0.8472-0.8505 | 6 |
| 3 | 28 | 37L | 37L | 25:23 | 0.8595 | 0.8567-0.8623 | 10 |
| 3 | 20 | 37L | 37L | 25:24 | 0.8604 | 0.8576-0.8632 | 10 |
| 3 | 21 | 37L | 37L | 25:34 | 0.8657 | 0.8629-0.8685 | 10 |
| 3 | 33 | 37L | 37L | 25:39 | 0.8678 | 0.865-0.8707 | 10 |
| 3 | 22 | 37L | 37L | 26:03 | 0.8821 | 0.8804-0.8837 | 6 |
| 3 | 36 | 37L | 37L | 27:41 | 0.9368 | 0.9351-0.9385 | 6 |
| 3 | 39 | 37L | 37L | 28:03 | 0.9496 | 0.9479-0.9513 | 6 |
| 3 | 38 | 37L | 37L | 28:40 | 0.9703 | 0.9686-0.972 | 6 |
| 3 | 35 | 37L | 37L | 29:08 | 0.9861 | 0.9844-0.9878 | 6 |
| 3 | 37 | 37L | 37L | 29:33 | 1.0006 | 0.9989-1.0023 | 6 |
| **Tetrachlorobiphenyls** | | | | | | | |
| 4 | 54L | 52L | 32L | 22:29 | 0.8249 | 0.8188-0.831 | 20 |
| 4 | 52L | 52L | 52L | 27:16 | 1.0000 | 0.9924-1.0076 | 25 |
| 4 | 79L | 81L | 81L/77L | 35:25 | 0.9717 | 0.9703-0.9731 | 6 |
| 4 | 81L | 52L | 52L | 36:27 | 1.3372 | 1.3311-1.3433 | 20 |
| 4 | 77L | 52L | 52L | 37:01 | 1.3582 | 1.3521-1.3643 | 20 |
| 4 | 54 | 54L | 54L | 22:30 | 1.0012 | 0.9975-1.0049 | 10 |
| 4 | 50 | 54L | 81L/77L | 24:47 | 1.1018 | 1.098-1.1055 | 10 |
| 4 | 53 | 54L | 81L/77L | 24:51 | 1.1039 | 1.1002-1.1076 | 10 |
| 4 | 45 | 54L | 81L/77L | 25:30 | 1.1328 | 1.1291-1.1365 | 10 |
| 4 | 51 | 54L | 81L/77L | 25:34 | 1.1368 | 1.1331-1.1405 | 10 |
| 4 | 46 | 54L | 81L/77L | 25:48 | 1.1478 | 1.1455-1.15 | 6 |
| 4 | 52 | 54L | 81L/77L | 27:18 | 1.2128 | 1.2106-1.215 | 6 |

| Cl No[1] | IUPAC No[2,3] | RT Ref[4] | Quantitation Reference[5] | RT[6] | RRT[7] | RRT Limit[8] | RT Win[9] (sec) |
|---|---|---|---|---|---|---|---|
| 4 | 73 | 54L | 81L/77L | 27:27 | 1.2201 | 1.2178-1.2223 | 6 |
| 4 | 43 | 54L | 81L/77L | 27:32 | 1.2249 | 1.2227-1.2271 | 6 |
| 4 | 69 | 54L | 81L/77L | 27:44 | 1.2344 | 1.2307-1.2381 | 10 |
| 4 | 49 | 54L | 81L/77L | 27:49 | 1.2357 | 1.232-1.2394 | 10 |
| 4 | 48 | 54L | 81L/77L | 28:06 | 1.2494 | 1.2472-1.2517 | 6 |
| 4 | 65 | 54L | 81L/77L | 28:18 | 1.2590 | 1.2553-1.2627 | 10 |
| 4 | 47 | 54L | 81L/77L | 28:21 | 1.2609 | 1.2572-1.2646 | 10 |
| 4 | 44 | 54L | 81L/77L | 28:22 | 1.2625 | 1.2588-1.2663 | 10 |
| 4 | 62 | 54L | 81L/77L | 28:39 | 1.2743 | 1.2706-1.278 | 10 |
| 4 | 75 | 54L | 81L/77L | 28:39 | 1.2739 | 1.2702-1.2776 | 10 |
| 4 | 59 | 54L | 81L/77L | 28:43 | 1.2762 | 1.2725-1.2799 | 10 |
| 4 | 42 | 54L | 81L/77L | 28:52 | 1.2843 | 1.2821-1.2865 | 6 |
| 4 | 41 | 54L | 81L/77L | 29:17 | 1.3009 | 1.2972-1.3046 | 10 |
| 4 | 71 | 54L | 81L/77L | 29:22 | 1.3059 | 1.3022-1.3096 | 10 |
| 4 | 40 | 54L | 81L/77L | 29:23 | 1.3065 | 1.3028-1.3102 | 10 |
| 4 | 64 | 54L | 81L/77L | 29:36 | 1.3174 | 1.3152-1.3197 | 6 |
| 4 | 72 | 81L | 81L/77L | 30:29 | 0.8358 | 0.8344-0.8371 | 6 |
| 4 | 68 | 81L | 81L/77L | 30:46 | 0.8441 | 0.8427-0.8455 | 6 |
| 4 | 57 | 81L | 81L/77L | 31:13 | 0.8559 | 0.8545-0.8573 | 6 |
| 4 | 58 | 81L | 81L/77L | 31:26 | 0.8625 | 0.8611-0.8639 | 6 |
| 4 | 67 | 81L | 81L/77L | 31:36 | 0.8671 | 0.8657-0.8685 | 6 |
| 4 | 63 | 81L | 81L/77L | 31:54 | 0.8746 | 0.8732-0.876 | 6 |
| 4 | 61 | 81L | 81L/77L | 32:09 | 0.8819 | 0.8791-0.8846 | 12 |
| 4 | 70 | 81L | 81L/77L | 32:12 | 0.8837 | 0.8809-0.8864 | 12 |
| 4 | 76 | 81L | 81L/77L | 32:14 | 0.8843 | 0.8816-0.8871 | 12 |
| 4 | 74 | 81L | 81L/77L | 32:18 | 0.8863 | 0.884-0.8886 | 10 |
| 4 | 66 | 81L | 81L/77L | 32:35 | 0.8935 | 0.8921-0.8949 | 6 |
| 4 | 55 | 81L | 81L/77L | 32:45 | 0.8983 | 0.897-0.8997 | 6 |
| 4 | 56 | 81L | 81L/77L | 33:15 | 0.9123 | 0.911-0.9137 | 6 |
| 4 | 60 | 81L | 81L/77L | 33:29 | 0.9185 | 0.9171-0.9198 | 6 |
| 4 | 80 | 81L | 81L/77L | 33:52 | 0.9293 | 0.9279-0.9307 | 6 |
| 4 | 79 | 81L | 81L/77L | 35:27 | 0.9723 | 0.9709-0.9736 | 6 |
| 4 | 78 | 81L | 81L/77L | 36:02 | 0.9881 | 0.9867-0.9895 | 6 |
| 4 | 81 | 81L | 81L | 36:29 | 1.0005 | 0.9991-1.0018 | 6 |
| 4 | 77 | 77L | 77L | 37:02 | 1.0005 | 0.9991-1.0018 | 6 |
| **Pentachlorobiphenyls** | | | | | | | |
| 5 | 104L | 101L | 101L | 28:15 | 0.8234 | 0.8185-0.8282 | 20 |
| 5 | 95L | 104L | 104L | 31:18 | 1.1080 | 1.105-1.1109 | 10 |
| 5 | 101L | 101L | 101L | 34:19 | 1.0000 | 0.9939-1.0061 | 25 |
| 5 | 111L | 101L | 101L | 37:03 | 1.0796 | 1.0748-1.0845 | 20 |
| 5 | 123L | 101L | 101L | 39:03 | 1.1381 | 1.1332-1.1429 | 20 |
| 5 | 118L | 101L | 101L | 39:23 | 1.1478 | 1.1429-1.1527 | 20 |
| 5 | 114L | 101L | 101L | 39:56 | 1.1637 | 1.1588-1.1685 | 20 |
| 5 | 105L | 101L | 101L | 40:35 | 1.1827 | 1.1779-1.1876 | 20 |
| 5 | 127L | 127L | 127L | 42:04 | 1.0000 | 0.995-1.005 | 25 |
| 5 | 126L | 101L | 101L | 43:43 | 1.2741 | 1.2692-1.2789 | 20 |
| 5 | 104 | 104L | 104L | 28:16 | 1.0010 | 0.998-1.0039 | 10 |
| 5 | 96 | 104L | 104L | 28:41 | 1.0141 | 1.0112-1.0171 | 10 |
| 5 | 103 | 104L | 104L | 30:40 | 1.0843 | 1.0825-1.0861 | 6 |
| 5 | 94 | 104L | 104L | 30:53 | 1.0932 | 1.0914-1.095 | 6 |
| 5 | 95 | 104L | 104L | 31:21 | 1.1084 | 1.1055-1.1114 | 10 |
| 5 | 100 | 104L | 104L | 31:34 | 1.1172 | 1.1143-1.1202 | 10 |
| 5 | 93 | 104L | 104L | 31:34 | 1.1176 | 1.1147-1.1206 | 10 |
| 5 | 102 | 104L | 104L | 31:42 | 1.1221 | 1.1192-1.1251 | 10 |
| 5 | 98 | 104L | 104L | 31:47 | 1.1253 | 1.1224-1.1283 | 10 |
| 5 | 88 | 104L | 104L | 32:09 | 1.1367 | 1.1332-1.1403 | 12 |
| 5 | 91 | 104L | 104L | 32:13 | 1.1406 | 1.1377-1.1436 | 10 |
| 5 | 84 | 104L | 104L | 32:26 | 1.1483 | 1.1465-1.1501 | 6 |
| 5 | 89 | 104L | 104L | 32:57 | 1.1652 | 1.1635-1.167 | 6 |
| 5 | 121 | 104L | 104L | 33:22 | 1.1809 | 1.1792-1.1827 | 6 |
| 5 | 92 | 123L | 104L | 33:45 | 0.8640 | 0.8628-0.8653 | 6 |
| 5 | 113 | 104L | 104L | 34:17 | 1.2124 | 1.2094-1.2153 | 10 |
| 5 | 90 | 104L | 104L | 34:20 | 1.2153 | 1.2124-1.2183 | 10 |
| 5 | 101 | 104L | 104L | 34:20 | 1.2156 | 1.2126-1.2185 | 10 |
| 5 | 83 | 104L | 104L | 34:50 | 1.2320 | 1.2285-1.2356 | 12 |
| 5 | 99 | 104L | 104L | 34:57 | 1.2372 | 1.2342-1.2401 | 10 |
| 5 | 112 | 104L | 104L | 35:03 | 1.2408 | 1.239-1.2425 | 6 |
| 5 | 119 | 104L | 104L | 35:27 | 1.2536 | 1.2489-1.2583 | 16 |
| 5 | 108 | 104L | 104L | 35:25 | 1.2535 | 1.2517-1.2553 | 6 |
| 5 | 86 | 104L | 104L | 35:26 | 1.2547 | 1.25-1.2594 | 16 |
| 5 | 97 | 104L | 104L | 35:27 | 1.2547 | 1.25-1.2594 | 16 |
| 5 | 125 | 104L | 104L | 35:31 | 1.2577 | 1.253-1.2624 | 16 |
| 5 | 87 | 104L | 104L | 35:34 | 1.2576 | 1.2546-1.2605 | 10 |

| Cl No[1] | IUPAC No[2,3] | RT Ref[4] | Quantitation Reference[5] | RT[6] | RRT[7] | RRT Limit[8] | RT Win[9] (sec) |
|---|---|---|---|---|---|---|---|
| 5 | 117 | 104L | 104L | 36:06 | 1.2779 | 1.2743-1.2814 | 12 |
| 5 | 116 | 104L | 104L | 36:12 | 1.2817 | 1.2781-1.2852 | 12 |
| 5 | 85 | 104L | 104L | 36:12 | 1.2804 | 1.2774-1.2833 | 10 |
| 5 | 110 | 104L | 104L | 36:20 | 1.2868 | 1.2839-1.2898 | 10 |
| 5 | 115 | 104L | 104L | 36:26 | 1.2897 | 1.2867-1.2926 | 10 |
| 5 | 82 | 104L | 104L | 36:42 | 1.2976 | 1.2959-1.2994 | 6 |
| 5 | 111 | 104L | 104L | 37:04 | 1.3123 | 1.3105-1.3141 | 6 |
| 5 | 120 | 104L | 104L | 37:33 | 1.3281 | 1.3263-1.3299 | 6 |
| 5 | 107 | 104L | 123L/114L/118L/105L/126L | 38:43 | 1.3703 | 1.3656-1.375 | 16 |
| 5 | 124 | 104L | 123L/114L/118L/105L/126L | 38:43 | 1.3692 | 1.3662-1.3721 | 10 |
| 5 | 109 | 104L | 123L/114L/118L/105L/126L | 38:57 | 1.3788 | 1.3759-1.3818 | 10 |
| 5 | 123 | 123L | 123L | 39:04 | 1.0007 | 0.9994-1.002 | 6 |
| 5 | 106 | 123L | 123L/114L/118L/105L/126L | 39:13 | 1.0038 | 1.0026-1.0051 | 6 |
| 5 | 118 | 118L | 118L | 39:25 | 1.0006 | 0.9993-1.0018 | 6 |
| 5 | 122 | 118L | 123L/114L/118L/105L/126L | 39:46 | 1.0093 | 1.008-1.0106 | 6 |
| 5 | 114 | 114L | 114L | 39:58 | 1.0007 | 0.9994-1.0019 | 6 |
| 5 | 105 | 105L | 105L | 40:37 | 1.0008 | 0.9996-1.0021 | 6 |
| 5 | 127 | 105L | 123L/114L/118L/105L/126L | 42:06 | 1.0374 | 1.0361-1.0386 | 6 |
| 5 | 126 | 126L | 126L | 43:43 | 1.0005 | 0.9994-1.0017 | 6 |
| **Hexachlorobiphenyls** | | | | | | | |
| 6 | 155L | 138L | 101L | 34:05 | 0.8013 | 0.7974-0.8053 | 20 |
| 6 | 153L | 167L | 156L/157L/167L/169L | 41:17 | 0.9055 | 0.9037-0.9073 | 10 |
| 6 | 138L | 138L | 138L | 42:32 | 1.0000 | 0.9804-1.0196 | 100 |
| 6 | 167L | 138L | 138L | 45:35 | 1.0715 | 1.0676-1.0754 | 20 |
| 6 | 156L | 138L | 138L | 46:46 | 1.0992 | 1.098-1.1004 | 6 |
| 6 | 157L | 138L | 138L | 46:46 | 1.0992 | 1.098-1.1004 | 6 |
| 6 | 169L | 138L | 138L | 50:02 | 1.1761 | 1.1749-1.1773 | 6 |
| 6 | 155 | 155L | 155L | 34:07 | 1.0010 | 0.9985-1.0034 | 10 |
| 6 | 152 | 155L | 155L | 34:20 | 1.0065 | 1.005-1.008 | 6 |
| 6 | 150 | 155L | 155L | 34:29 | 1.0111 | 1.0096-1.0125 | 6 |
| 6 | 136 | 155L | 155L | 34:52 | 1.0222 | 1.0207-1.0236 | 6 |
| 6 | 145 | 155L | 155L | 35:10 | 1.0311 | 1.0296-1.0326 | 6 |
| 6 | 148 | 155L | 155L | 36:42 | 1.0761 | 1.0746-1.0775 | 6 |
| 6 | 151 | 155L | 155L | 37:17 | 1.0933 | 1.0909-1.0958 | 10 |
| 6 | 135 | 155L | 155L | 37:21 | 1.0951 | 1.0927-1.0976 | 10 |
| 6 | 154 | 155L | 155L | 37:33 | 1.1017 | 1.0993-1.1042 | 10 |
| 6 | 144 | 155L | 155L | 37:53 | 1.1108 | 1.1093-1.1122 | 6 |
| 6 | 147 | 155L | 156L/157L/167L/169L | 38:14 | 1.1219 | 1.1195-1.1244 | 10 |
| 6 | 149 | 155L | 156L/157L/167L/169L | 38:15 | 1.1214 | 1.1189-1.1238 | 10 |
| 6 | 134 | 155L | 156L/157L/167L/169L | 38:26 | 1.1280 | 1.1255-1.1304 | 10 |
| 6 | 143 | 155L | 156L/157L/167L/169L | 38:33 | 1.1303 | 1.1279-1.1328 | 10 |
| 6 | 139 | 155L | 156L/157L/167L/169L | 38:51 | 1.1389 | 1.1365-1.1414 | 10 |
| 6 | 140 | 155L | 156L/157L/167L/169L | 38:51 | 1.1399 | 1.1374-1.1423 | 10 |
| 6 | 131 | 155L | 156L/157L/167L/169L | 39:03 | 1.1459 | 1.1444-1.1474 | 6 |
| 6 | 142 | 155L | 156L/157L/167L/169L | 39:14 | 1.1505 | 1.149-1.152 | 6 |
| 6 | 132 | 155L | 156L/157L/167L/169L | 39:31 | 1.1588 | 1.1564-1.1613 | 10 |
| 6 | 133 | 155L | 156L/157L/167L/169L | 40:02 | 1.1736 | 1.1722-1.1751 | 6 |
| 6 | 165 | 167L | 156L/157L/167L/169L | 40:26 | 0.8868 | 0.8857-0.8879 | 6 |
| 6 | 146 | 167L | 156L/157L/167L/169L | 40:40 | 0.8921 | 0.891-0.8932 | 6 |
| 6 | 161 | 167L | 156L/157L/167L/169L | 40:50 | 0.8955 | 0.8944-0.8966 | 6 |
| 6 | 153 | 167L | 156L/157L/167L/169L | 41:19 | 0.9059 | 0.9041-0.9078 | 10 |
| 6 | 168 | 167L | 156L/157L/167L/169L | 41:21 | 0.9071 | 0.9053-0.909 | 10 |
| 6 | 141 | 167L | 156L/157L/167L/169L | 41:30 | 0.9104 | 0.9093-0.9115 | 6 |
| 6 | 130 | 167L | 156L/157L/167L/169L | 41:55 | 0.9193 | 0.9183-0.9204 | 6 |
| 6 | 137 | 167L | 156L/157L/167L/169L | 42:09 | 0.9247 | 0.9236-0.9258 | 6 |
| 6 | 164 | 167L | 156L/157L/167L/169L | 42:15 | 0.9269 | 0.9258-0.928 | 6 |
| 6 | 138 | 167L | 156L/157L/167L/169L | 42:33 | 0.9338 | 0.9312-0.9364 | 14 |
| 6 | 163 | 167L | 156L/157L/167L/169L | 42:34 | 0.9342 | 0.9316-0.9367 | 14 |
| 6 | 129 | 167L | 156L/157L/167L/169L | 42:39 | 0.9352 | 0.9326-0.9377 | 14 |
| 6 | 160 | 167L | 156L/157L/167L/169L | 42:45 | 0.9379 | 0.936-0.9397 | 10 |
| 6 | 158 | 167L | 156L/157L/167L/169L | 42:57 | 0.9424 | 0.9413-0.9434 | 6 |
| 6 | 166 | 167L | 156L/157L/167L/169L | 43:50 | 0.9614 | 0.9596-0.9632 | 10 |
| 6 | 128 | 167L | 156L/157L/167L/169L | 43:52 | 0.9621 | 0.9603-0.9639 | 10 |
| 6 | 159 | 167L | 156L/157L/167L/169L | 44:51 | 0.9836 | 0.9825-0.9846 | 6 |
| 6 | 162 | 167L | 156L/157L/167L/169L | 45:08 | 0.9899 | 0.9888-0.991 | 6 |
| 6 | 167 | 167L | 167L | 45:37 | 1.0005 | 0.9994-1.0016 | 6 |
| 6 | 156 | 156L | 156L/157L | 46:46 | 0.9999 | 0.9988-1.001 | 6 |
| 6 | 157 | 157L | 156L/157L | 46:48 | 1.0008 | 0.999-1.0026 | 10 |
| 6 | 169 | 169L | 169L | 50:02 | 1.0003 | 0.9993-1.0013 | 6 |
| **Heptachlorobiphenyls** | | | | | | | |
| 7 | 188L | 180L | 180L | 39:55 | 0.8287 | 0.8253-0.8322 | 20 |
| 7 | 178L | 180L | 180L | 42:59 | 0.8926 | 0.8892-0.8961 | 20 |
| 7 | 180L | 180L | 180L | 48:10 | 1.0000 | 0.9827-1.0173 | 100 |

| Cl No[1] | IUPAC No[2,3] | RT Ref[4] | Quantitation Reference[5] | RT[6] | RRT[7] | RRT Limit[8] | RT Win[9] (sec) |
|---|---|---|---|---|---|---|---|
| 7 | 170L | 180L | 194L | 49:26 | 1.0265 | 1.023-1.0299 | 20 |
| 7 | 189L | 180L | 180L | 52:35 | 1.0918 | 1.0884-1.0953 | 20 |
| 7 | 188 | 188L | 188L | 39:56 | 1.0007 | 0.9994-1.0019 | 6 |
| 7 | 179 | 188L | 188L/170L | 40:17 | 1.0090 | 1.0078-1.0103 | 6 |
| 7 | 184 | 188L | 188L/170L | 40:49 | 1.0224 | 1.0212-1.0237 | 6 |
| 7 | 176 | 188L | 188L/170L | 41:11 | 1.0316 | 1.0303-1.0328 | 6 |
| 7 | 186 | 188L | 188L/170L | 41:39 | 1.0434 | 1.0422-1.0447 | 6 |
| 7 | 178 | 188L | 188L/170L | 43:02 | 1.0779 | 1.0767-1.0792 | 6 |
| 7 | 175 | 188L | 188L/170L | 43:41 | 1.0939 | 1.0927-1.0952 | 6 |
| 7 | 187 | 188L | 188L/170L | 43:57 | 1.1008 | 1.0995-1.102 | 6 |
| 7 | 182 | 188L | 188L/170L | 44:08 | 1.1058 | 1.1045-1.107 | 6 |
| 7 | 183 | 188L | 188L/170L | 44:35 | 1.1165 | 1.1152-1.1177 | 6 |
| 7 | 185 | 188L | 188L/170L | 44:41 | 1.1191 | 1.1179-1.1204 | 6 |
| 7 | 174 | 188L | 188L/170L | 44:47 | 1.1221 | 1.1208-1.1233 | 6 |
| 7 | 177 | 188L | 188L/170L | 45:16 | 1.1336 | 1.1323-1.1348 | 6 |
| 7 | 181 | 188L | 188L/170L | 45:40 | 1.1439 | 1.1426-1.1451 | 6 |
| 7 | 171 | 188L | 188L/170L | 45:54 | 1.1496 | 1.1475-1.1517 | 10 |
| 7 | 173 | 188L | 188L/170L | 45:51 | 1.1485 | 1.1473-1.1498 | 6 |
| 7 | 172 | 189L | 188L/170L | 47:32 | 0.9037 | 0.9027-0.9046 | 6 |
| 7 | 192 | 189L | 188L/170L | 47:49 | 0.9093 | 0.9083-0.9102 | 6 |
| 7 | 193 | 189L | 188L/170L | 48:07 | 0.9152 | 0.9142-0.9161 | 6 |
| 7 | 180 | 189L | 188L/170L | 48:10 | 0.9161 | 0.9152-0.9171 | 6 |
| 7 | 191 | 189L | 188L/170L | 48:33 | 0.9230 | 0.922-0.9239 | 6 |
| 7 | 170 | 189L | 170L | 49:28 | 0.9406 | 0.9397-0.9416 | 6 |
| 7 | 190 | 189L | 188L/170L | 50:00 | 0.9508 | 0.9498-0.9517 | 6 |
| 7 | 189 | 189L | 189L | 52:36 | 1.0005 | 0.9996-1.0015 | 6 |
| **Octachlorobiphenyls** | | | | | | | |
| 8 | 202L | 194L | 194L | 45:21 | 0.8289 | 0.8258-0.8319 | 20 |
| 8 | 194L | 194L | 194L | 54:42 | 1.0000 | 0.9962-1.0038 | 25 |
| 8 | 205L | 194L | 194L | 55:11 | 1.0087 | 1.0041-1.0132 | 30 |
| 8 | 202 | 202L | 202L | 45:22 | 1.0005 | 0.9987-1.0023 | 10 |
| 8 | 201 | 202L | 202L | 46:19 | 1.0213 | 1.0202-1.0224 | 6 |
| 8 | 204 | 202L | 202L | 47:00 | 1.0364 | 1.0353-1.0375 | 6 |
| 8 | 197 | 202L | 202L | 47:14 | 1.0413 | 1.0402-1.0424 | 6 |
| 8 | 200 | 202L | 202L | 47:21 | 1.0439 | 1.0427-1.045 | 6 |
| 8 | 198 | 202L | 202L | 50:08 | 1.1052 | 1.1034-1.1071 | 10 |
| 8 | 199 | 202L | 202L | 50:10 | 1.1062 | 1.1044-1.108 | 10 |
| 8 | 196 | 205L | 202L | 50:50 | 0.9211 | 0.9202-0.922 | 6 |
| 8 | 203 | 205L | 202L | 51:02 | 0.9249 | 0.924-0.9258 | 6 |
| 8 | 195 | 205L | 205L | 52:23 | 0.9492 | 0.9483-0.9501 | 6 |
| 8 | 194 | 205L | 205L | 54:45 | 0.9918 | 0.9909-0.9928 | 6 |
| 8 | 205 | 205L | 205L | 55:12 | 1.0005 | 0.9996-1.0014 | 6 |
| **Nonachlorobiphenyls** | | | | | | | |
| 9 | 208L | 194L | 194L | 52:06 | 0.9525 | 0.9494-0.9555 | 20 |
| 9 | 206L | 194L | 194L | 56:57 | 1.0409 | 1.0363-1.0455 | 30 |
| 9 | 208 | 208L | 208L | 52:08 | 1.0004 | 0.9995-1.0014 | 6 |
| 9 | 207 | 208L | 208L/206L | 53:05 | 1.0184 | 1.0175-1.0194 | 6 |
| 9 | 206 | 206L | 206L | 56:57 | 1.0003 | 0.9994-1.0012 | 6 |
| **Decachlorobiphenyls** | | | | | | | |
| 10 | 209L | 194L | 194L | 58:34 | 1.0706 | 1.066-1.0751 | 30 |
| 10 | 209 | 209L | 209L | 58:34 | 1.0003 | 0.9994-1.0011 | 6 |

1. Number of chlorines on congener.
2. Suffix "L" indicates labeled compound.
3. IUPAC Number per Table 2 of Method 1668A.
4. Retention time reference that is used to locate target congener.
5. Quantitation reference that is used to calculate the concentration of the target congener or labeled standard.
6. Retention time of target congener.
7. RRT between the RT for the congener and RT for the reference.
8. Nominal limits based on an ± 0.5% of the RRT, adjusted for the nearest eluted isomer.
9. RT window width for congener or group of two or more congeners.
10. Labeled congeners that form the quantitation reference. Areas from the exact m/z's of the congeners listed in the quantitation reference are summed, and divided by the number of congeners in the quantitation reference. For example, for congener 10, the areas at the exact m/z's for 4L and 15L are summed and the sum is divided by 2 (because there are 2 congeners in the quantitation reference).

Table 3

Low Calibration Levels (LCLs) Based on Final Extract Volumes

| | | 20 µL Extract Volume | | 100µL Extract Volume | |
|---|---|---|---|---|---|
| Analyte | Minimum Cal. Level CS0.5 (ng/mL) | Water 1L (ng/L) | Solids and Tissues 10g (ng/g) | Water 1L (ng/L) | Solids and Tissues 10g (ng/g) |
| Monochlorobiphenyls | 0.5 | 0.01[1] | 0.001[1] | 0.05 | 0.005 |
| Dichlorobiphenyls | 0.5 | 0.01[1] | 0.001[1] | 0.05 | 0.005 |
| Trichlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Tetrachlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Pentachlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Hexachlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Heptachlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Octachlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Nonachlorobiphenyls | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |
| Decachlorobiphenyl | 0.5 | 0.01 | 0.001 | 0.05 | 0.005 |

1. This value reflects the LCL. Reliable detection at this level may not be attained due to evaporative loss in adjusting the extract volume to 20 µL for these homolog groups.

2. The values for solids and tissues reflect the LCLs for Protocol 1 as described in section 11.4. If the sample is prepared by another protocol described in that section, the LCLs shown in this table are multiplied by the EML multiplier, shown in the section 11.4 table.

Table 4

Estimated Minimum Levels – Matrix and Concentration

| Parameter | Water ng/L | Solids ng/g | Tissues ng/g | Solid Wastes ng/g | 100 uL Extract ng/mL |
|---|---|---|---|---|---|
| PCB 1 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 2 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 3 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 4 | 0.060 | 0.02 | 0.02 | 0.02 | 2.0 |
| PCB 5 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 6 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 7 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 8 | 0.060 | 0.02 | 0.02 | 0.02 | 2.0 |
| PCB 9 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 10 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 11 | 0.060 | 0.02 | 0.02 | 0.02 | 2.0 |
| PCB 12/PCB 13 | 0.060 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 14 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 15 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 16 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 17 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 18/PCB 30 | 0.060 | 0.02 | 0.02 | 0.02 | 2.0 |
| PCB 19 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 20/PCB 28 | 0.040 | 0.02 | 0.02 | 0.02 | 2.0 |
| PCB 21/PCB33 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 22 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 23 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 24 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 25 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 26/PCB 29 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 27 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 31 | 0.040 | 0.02 | 0.02 | 0.02 | 2.0 |
| PCB 32 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 34 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 35 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 36 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 37 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 38 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 39 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 40/PCB41/PCB 71 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 42 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 43/PCB 73 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 44/PCB 47/PCB 65 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 45/PCB 51 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 46 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 48 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 49/PCB 69 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 50/PCB 53 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 52 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 54 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 55 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 56 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 57 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 58 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 59/PCB 62/PCB 75 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 60 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 61/PCB 70/PCB 74/PCB 76 | 0.040 | 0.02 | 0.02 | 0.02 | 2.0 |

| Parameter | Water ng/L | Solids ng/g | Tissues ng/g | Solid Wastes ng/g | 100 uL Extract ng/mL |
|---|---|---|---|---|---|
| PCB 63 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 64 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 66 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 67 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 68 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 72 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 77 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 78 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 79 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 80 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 81 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 82 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 83 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 84 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 85/PCB 116/PCB 117 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 86/PCB 87/PCB 97/PCB 109/PCB 119/PCB 125 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 88/PCB 91 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 89 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 90/PCB 101/PCB 113 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 92 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 93/PCB 100 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 94 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 95 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 96 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 98/PCB 102 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 99/PCB 112 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 103 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 104 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 105 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 106 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 107 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 108/PCB 124 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 110/PCB 115 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 111 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 114 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 118 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 120 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 121 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 122 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 123 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 126 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 127 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 128/PCB 166 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 129/PCB 138/PCB 163 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 130 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 131 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 132 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 133 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 134/PCB 143 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 135/PCB 151 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 136 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 137/PCB 164 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 139/PCB 140 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 141 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 142 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 144 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 145 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 146 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |

| Parameter | Water ng/L | Solids ng/g | Tissues ng/g | Solid Wastes ng/g | 100 uL Extract ng/mL |
|---|---|---|---|---|---|
| PCB 147/PCB 149 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 148 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 150 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 152 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 153/PCB 168 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 154 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 155 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 156/PCB 157 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 158 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 159 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 160 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 161 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 162 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 165 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 167 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 169 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 170 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 171/PCB 173 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 172 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 174 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 175 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 176 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 177 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 178 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 179 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 180/PCB 193 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 181 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 182 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 183/PCB 185 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 184 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 186 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 187 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 188 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 189 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 190 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 191 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 192 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 194 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 195 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 196 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 197/PCB 200 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 198/PCB 199 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 201 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 202 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 203 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 204 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 205 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 206 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 207 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 208 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |
| PCB 209 | 0.040 | 0.01 | 0.01 | 0.01 | 1.0 |

The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures The values for solids, tissues and solid wastes reflect the EMLs for Protocol 1 as described in section 11.4. If the sample is prepared by another protocol described in that section, the LCLs shown in this table are multiplied by the EML multiplier, shown in the section 11.4 table. The EMLs are based on the mean plus 2 standard deviations for matrix-pooled historical blank data and calibration data obtained while performing EPA 1668A. The survey period was fourteen months, ending in February 2004. Individual EMLs may be adjusted to reflect more recent data.

# Table 5

## Concentration of Stock and Spiking Solutions Containing PCBs and Labeled Compounds

| PCB Congener | BZ/ IUPAC | Standard Source | Catalog Number | Solution concentration (ng/mL) Labeled compound Stock[1] | Labeled compound Spiking[2] | PAR Stock[3] | PAR Spiking[4] |
|---|---|---|---|---|---|---|---|
| 2-MoCB | 1 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 4-MoCB | 3 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2'-DiCB | 4 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 4,4'-DiCB | 15 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',6-TrCB | 19 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 3,4,4'-TrCB | 37 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',6,6'-TeCB | 54 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 3,3',4,4'-TeCB | 77 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 3,4,4',5-TeCB | 81 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',4,6,6'-PeCB | 104 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3,3',4,4'-PeCB | 105 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3,4,4',5-PeCB | 114 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3',4,4',5-PeCB | 118 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2',3,4,4',5-PeCB | 123 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 3,3',4,4',5-PeCB | 126 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',4,4',6,6'-HxCB | 155 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3,3',4,4',5-HxCB | 156 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3,3',4,4',5'-HxCB | 157 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3',4,4',5,5'-HxCB | 167 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 3,3',4,4',5,5'-HxCB | 169 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',3,3',4,4',5-HpCB | 170 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',3,4,4',5,5'-HpCB | 180 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',3,4',5,6,6'-HpCB | 188 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3,3',4,4',5,5'-HpCB | 189 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',3,3',5,5',6,6'-OcCB | 202 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,3,3',4,4',5,5',6-OcCB | 205 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',3,3',4,4',5,5',6-NoCB | 206 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| 2,2',3,3',4',5,5',6,6'-NoCB | 208 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| DeCB | 209 | AccuStd | S-99994-4x | --- | --- | 4000 | 1.0/5.0 |
| All other CB congeners | NA | AccuStd | S-99994-4x | | | 4000 | 1.0/5.0 |
| **Labeled Internal Standards** | | | | | | | |
| $^{13}C_{12}$-2-chlorobiphenyl | 1L | Cambridge | EC-4908 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-4-chlorobiphenyl | $3L_{12}$ | Cambridge | EC-4990 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2'-dichlorobiphenyl | 4L | Cambridge | EC-4911 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-4,4'-dichlorobiphenyl | 15L | Cambridge | EC-1402 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',6-trichlorobiphenyl | 19L | Cambridge | EC-4909 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-3,4,4'-trichlorobiphenyl | 37L | Cambridge | EC-4901 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl | 54L | Cambridge | EC-4912 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl | 77L | Cambridge | EC-1404 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl | 81L | Cambridge | EC-1412 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl | 104L | Cambridge | EC-4910 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl | 105L | Cambridge | EC-1420 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl - | 114L | Cambridge | EC-4902 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl | 118L | Cambridge | EC-1435 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl | 123L | Cambridge | EC-4904 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl | 126L | Cambridge | EC-1425 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl | 155L | Cambridge | EC-4167 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl | 156L | Cambridge | EC-1422 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl | 157L | Cambridge | EC-4051 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl | 167L | Cambridge | EC-4050 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl | 169L | Cambridge | EC-1416 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl | 170L | Cambridge | EC-4905 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl | 188L | Cambridge | EC-4913 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl | 189L | Cambridge | EC-1409 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl | 202L | Cambridge | EC-1408 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl | 205L | Cambridge | EC-4199 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl | 206L | Cambridge | EC-4900 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl | 208L | Cambridge | EC-1419 | 1000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl | 209L | Cambridge | EC-1410 | 1000 | 2.0/10 | --- | --- |

## Table 5 Continued

| PCB Congener | BZ/ IUPAC | Standard Source | Catalog Number | Solution concentration (ng/mL) Labeled compound Stock | Labeled compound Spiking | PAR Stock | PAR Spiking |
|---|---|---|---|---|---|---|---|
| **Labeled Recovery Standards[5]** | | | | | | | |
| $^{13}C_{12}$-2,5-dichlorobiphenyl | 9L | Cambridge | EC-4165 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,4',5-trichlorobiphenyl | 31L | Wellington | MBP-31 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,4',6-trichlorobiphenyl | 32L | Cambridge | EC-4163 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl | 52L | Cambridge | EC-1424 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl | 101L | Cambridge | EC-1405 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl | 127L | Cambridge | EC-1421 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl | 138L | Cambridge | EC-1436 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl | 180L | Cambridge | EC-1407 | 1000 | 100 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl | 194L | Cambridge | EC-1418 | 1000 | 100 | --- | --- |
| **Cleanup Standards[6]** | | | | | | | |
| $^{13}C_{12}$-2,4,4'-trichlorobiphenyl | 28L | Cambridge | EC-1413 | 5000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl | 111L | Cambridge | EC-1415 | 5000 | 2.0/10 | --- | --- |
| $^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl | 178L | Cambridge | EC-1417 | 5000 | 2.0/10 | --- | --- |
| **Labeled Surrogate Standards[7]** | | | | | | | |
| $^{13}C_{12}$-2,4'-dichlorobiphenyl | 8L | Cambridge | EC-5095 | 5000 | 50 | --- | --- |
| $^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl | 79L | Cambridge | EC-5048 | 5000 | 50 | --- | --- |
| $^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl | 95L | Wellington | MBP-95 | 5000 | 50 | --- | --- |
| $^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl | 153L | Cambridge | EC-1406 | 5000 | 50 | --- | --- |

Notes:

1. Section 7.12.5.2– prepared in nonane and diluted to prepare spiking solution
2. Section 7.12.8– prepared in acetone from stock solution. Concentrations listed are for 20µL and 100µL final extract volumes.
3. Section 7.12.5.1 – prepared in nonane and diluted to prepare spiking solution.
4. Section 7.12.7– prepared in acetone from stock solution. Concentrations listed are for 20µL and 100µL final extract volumes.
5. Section 7.12.11– prepared in nonane and added to concentrated extract prior to injection.
6. Section 7.12.9– prepared in hexane and added to extract prior to cleanup. Concentrations listed are for 20µL and 100µL final extract volumes
7. Section 7.12.10– prepared in nonane and added to XAD tube prior to sampling.

# Table 6
## Concentration of PCBs in Calibration Solutions

| Analyte Type | BZ/IUPAC[1] | CS 0.5 ng/mL | CS 1 ng/mL | CS 2 ng/mL | CS 3[2] ng/mL | CS 4 ng/mL | CS 5 ng/mL |
|---|---|---|---|---|---|---|---|
| **Congeners** | | | | | | | |
| 2-MoCB | 1 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 4-MoCB | 3 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2'-DiCB | 4 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 4,4'-DiCB | 15 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',6'-TrCB | 19 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 3,4,4'-TrCB | 37 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',6,6'-TeCB | 54 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 3,3',4,4'-TeCB | 77 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 3,4,4',5-TeCB | 81 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',4,6,6'-PeCB | 104 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3,3',4,4'-PeCB | 105 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3,4,4',5-PeCB | 114 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3',4,4',5-PeCB | 118 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2',3,4,4',5-PeCB | 123 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 3,3',4,4',5-PeCB | 126 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',4,4',6,6'-HxCB | 155 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3,3',4,4',5-HxCB | 156 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3,3',4,4',5'-HxCB | 157 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3',4,4',5,5'-HxCB | 167 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 3,3',4,4',5,5'-HxCB | 169 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',3,4',5,6,6'-HpCB | 188 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3,3',4,4',5,5'-HpCB | 189 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',3,3',5,5',6,6'-OcCB | 202 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,3,3',4,4',5,5',6-OcCB | 205 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',3,3',4,4',5,5',6-NoCB | 206 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| 2,2',3,3',4',5,5',6,6'-NoCB | 208 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| DeCB | 209 | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| All other CB congeners | | 0.5 | 1.0 | 5.0 | 50 | 400 | 2000 |
| **Labeled Congeners** | | | | | | | |
| $^{13}C_{12}$-2-MoCB | 1L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-4-MoCB | 3L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2'-DiCB | 4L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-4,4'-DiCB | 15L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',6-TrCB | 19L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-3,4,4'-TrCB | 37L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',6,6'-TeCB | 54L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-3,3',4,4'-TeCB | 77L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-3,4,4',5-TeCB | 81L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',4,6,6'-PeCB | 104L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3,3',4,4'-PeCB | 105L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3,4,4',5-PeCB | 114L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3',4,4',5-PeCB | 118L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2',3,4,4',5-PeCB | 123L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-3,3',4,4',5-PeCB | 126L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',4,4',6,6'-HxCB | 155L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3,3',4,4',5-HxCB | 156L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3,3',4,4',5'-HxCB | 157L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3',4,4',5,5'-HxCB | 167L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-3,3',4,4',5,5'-HxCB | 169L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,3',4,4',5-HpCB | 170L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB | 188L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB | 189L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB | 202L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB | 205L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB | 206L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB | 208L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-DeCB | 209L | 100 | 100 | 100 | 100 | 100 | 100 |
| **Cleanup Standards** | | | | | | | |
| $^{13}C_{12}$-2,4,4'-TriCB | 28L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |
| $^{13}C_{12}$-2,3,3',5,5'-PeCB | 111L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |
| $^{13}C_{12}$-2,2',3,3',5,5',6-HpCB | 178L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |

Table 6 Continued

| Analyte Type | BZ/IUPAC[1] | CS 0.5 ng/mL | CS 1 ng/mL | CS 2 ng/mL | CS 3[2] ng/mL | CS 4 ng/mL | CS 5 ng/mL |
|---|---|---|---|---|---|---|---|
| **Recovery Standards** | | | | | | | |
| $^{13}C_{12}$-2,5-DiCB | 9L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,4',5-TriCB | 31L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,4',6-TriCB | 32L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',5,5'-TeCB | 52L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',4',5,5'-PeCB | 101L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-3,3',4,5,5'-PeCB | 127L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3',4,4',5'-HxCB | 138L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB | 180L | 100 | 100 | 100 | 100 | 100 | 100 |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB | 194L | 100 | 100 | 100 | 100 | 100 | 100 |
| **Labeled Sampling Surrogates** | | | | | | | |
| $^{13}C_{12}$-2,4'-DiCB | 8L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |
| $^{13}C_{12}$-3,3',4,5'-TeCB | 79L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |
| $^{13}C_{12}$-2,2',3,5',6-PeCB | 95L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |
| $^{13}C_{12}$-2,2',4,4',5,5'-HxCB | 153L | 0.5 | 1.0 | 5.0 | 50 | 400 | -- |

Notes:
1. Suffix "L" indicates labeled compound
2. Section 15.3, calibration verification solution

Table 7

GC Window Defining Mixture

SPB-Octyl

| Congener Group | First Eluted | | Last Eluted | |
|---|---|---|---|---|
| Mono | 1 | 2- | 3 | 4- |
| Di | 4 | 2,2'- | 15 | 4,4'- |
| Tri | 19 | 2,2',6- | 37 | 3,4,4'- |
| Tetra | 54 | 2,2',6,6'- | 77 | 3,3',4,4'- |
| Penta | 104 | 2,2',4,6,6'- | 126 | 3,3',4,4',5- |
| Hexa | 155 | 2,2',4,4',6,6'- | 169 | 3,3',4,4',5,5'- |
| Hepta | 188 | 2,2',3,4',5,6,6'- | 189 | 2,3,3',4,4',5,5'- |
| Octa | 202 | 2,2',3,3',5,5',6,6'- | 205 | 2,3,3',4,4',5,5',6- |
| Nona | 208 | 2,2',3,3',4,5,5',6,6'- | 206 | 2,2',3,3',4,4',5,5',6- |
| Deca | 209 | 2,2',3,3',4,4',5,5',6,6'- | 209 | 2,2',3,3',4,4',5,5',6,6'- |

SPB-Octyl Resolution Test Compounds

| | |
|---|---|
| 23 | 2,3,5-trichlorobiphenyl |
| 34 | 2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl) |
| 182 | 2,2',3,4,4',5,6'-heptachlorobiphenyl |
| 187 | 2,2',3,4',5,5',6-heptachlorobiphenyl |

Table 8

Ions Monitored for HRGC/HRMS Analysis of PCBs

| Descriptor | Accurate Mass | Ion ID | Elemental Composition | Analyte |
|---|---|---|---|---|
| 1 | 180.9888 | Lock | $C_4F_7$ | PFK |
| | 188.0393 | M | $C_{12}H_9{}^{35}Cl$ | Mono |
| | 190.0363 | M+2 | $C_{12}H_9{}^{37}Cl$ | Mono |
| | 200.0795 | M | $^{13}C_{12}H_9{}^{35}Cl$ | Mono-13C12 |
| | 202.0766 | M+2 | $^{13}C_{12}H_9{}^{37}Cl$ | Mono-13C12 |
| | 222.0003 | M | $C_{12}H_8{}^{35}Cl_2$ | Di |
| | 223.9974 | M+2 | $C_{12}H_8{}^{35}Cl^{37}Cl$ | Di |
| | 234.0406 | M | $^{13}C_{12}H_8{}^{35}Cl_2$ | Di-13C |
| | 236.0376 | M+2 | $^{13}C_{12}H_8{}^{35}Cl^{37}Cl$ | Di-13C |
| | 255.9613 | M | $C_{12}H_7{}^{35}Cl_3$ | Tri |
| | 257.9584 | M+2 | $C_{12}H_7{}^{35}Cl_2{}^{37}Cl$ | Tri |
| | 268.0016 | M | $^{13}C_{12}H_7{}^{35}Cl_3$ | Tri-13C |
| | 269.9986 | M+2 | $^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$ | Tri-13C |
| | 280.9824 | QC | $C_6F_{11}$ | PFK |
| | 289.9224 | M | $C_{12}H_6{}^{35}Cl_4$ | Tetra |
| | 291.9194 | M+2 | $C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | Tetra |
| | 301.9626 | M | $^{13}C_{12}H_6{}^{35}Cl_4$ | Tetra-13C |
| | 303.9597 | M+2 | $^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | Tetra-13C |
| 2 | 255.9613 | M | $C_{12}H_7{}^{35}Cl_3$ | Tri |
| | 257.9584 | M+2 | $C_{12}H_7{}^{35}Cl_2{}^{37}Cl$ | Tri |
| | 268.0016 | M | $^{13}C_{12}H_7{}^{35}Cl_3$ | Tri-13C |
| | 268.9824 | Lock | $C_5F_{11}$ | PFK |
| | 269.9986 | M+2 | $^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$ | Tri-13C |
| | 289.9224 | M | $C_{12}H_6{}^{35}Cl_4$ | Tetra |
| | 291.9194 | M+2 | $C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | Tetra |
| | 301.9626 | M | $^{13}C_{12}H_6{}^{35}Cl_4$ | Tetra-13C |
| | 303.9597 | M+2 | $^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | Tetra-13C |
| | 325.8804 | M+2 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | Penta |
| | 327.8775 | M+4 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ | Penta |
| | 337.9207 | M+2 | $^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | Penta-13C |
| | 339.9178 | M+4 | $^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ | Penta-13C |
| | 359.8415 | M+2 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | Hexa |
| | 361.8385 | M+4 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$ | Hexa |
| | 371.8817 | M+2 | $^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | Hexa-13C |
| | 373.8788 | M+4 | $^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$ | Hexa-13C |
| | 380.9760 | QC | $C_{10}F_{14}$ | PFK |

Table 8 Continued

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

| Descriptor | Accurate Mass | Ion ID | Elemental Composition | Analyte |
|---|---|---|---|---|
| 3 | 325.8804 | M+2 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | Penta |
| | 327.8775 | M+4 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ | Penta |
| | 337.9207 | M+2 | $^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | Penta-13C |
| | 339.9178 | M+4 | $^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ | Penta-13C |
| | 342.9792 | Lock | $C_8F_{13}$ | PFK |
| | 359.8415 | M+2 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | Hexa |
| | 361.8385 | M+4 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$ | Hexa |
| | 371.8817 | M+2 | $^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | Hexa-13C |
| | 373.8788 | M+4 | $^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$ | Hexa-13C |
| | 393.8025 | M+2 | $C_{12}H_3{}^{35}Cl_6{}^{37}Cl$ | Hepta |
| | 395.7995 | M+4 | $C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$ | Hepta |
| | 405.8428 | M+2 | $^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$ | Hepta-13C |
| | 407.8398 | M+4 | $^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$ | Hepta-13C |
| | 427.7635 | M+2 | $C_{12}H_2{}^{35}Cl_7{}^{37}Cl$ | Octa |
| | 429.7606 | M+4 | $C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$ | Octa |
| | 430.9728 | QC | $C_9F_{17}$ | PFK |
| | 439.8038 | M+2 | $^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$ | Octa-13C |
| | 441.8008 | M+4 | $^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$ | Octa-13C |
| 4 | 393.8025 | M+2 | $C_{12}H_3{}^{35}Cl_6{}^{37}Cl$ | Hepta |
| | 395.7995 | M+4 | $C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$ | Hepta |
| | 404.9760 | Lock | $C_{10}F_{15}$ | PFK |
| | 405.8428 | M+2 | $^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$ | Hepta-13C |
| | 407.8398 | M+4 | $^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$ | Hepta-13C |
| | 427.7635 | M+2 | $C_{12}H_2{}^{35}Cl_7{}^{37}Cl$ | Octa |
| | 429.7606 | M+4 | $C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$ | Octa |
| | 439.8038 | M+2 | $^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$ | Octa-13C |
| | 441.8008 | M+4 | $^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$ | Octa-13C |
| | 461.7246 | M+2 | $C_{12}H^{35}Cl_7{}^{37}Cl_2$ | Nona |
| | 463.7216 | M+4 | $C_{12}H^{35}Cl_6{}^{37}Cl_3$ | Nona |
| | 473.7648 | M+2 | $^{13}C_{12}H^{35}Cl_7{}^{37}Cl_2$ | Nona-13C |
| | 475.7619 | M+4 | $^{13}C_{12}H^{35}Cl_6{}^{37}Cl_3$ | Nona-13C |
| | 495.6856 | M+2 | $C_{12}{}^{35}Cl_8{}^{37}Cl_2$ | Deca |
| | 497.6826 | M+4 | $C_{12}{}^{35}Cl_7{}^{37}Cl_3$ | Deca |
| | 504.9697 | QC | $C_{12}F_{19}$ | PFK |
| | 507.7258 | M+2 | $^{13}C_{12}{}^{35}Cl_8{}^{37}Cl_2$ | Deca-13C |
| | 509.7229 | M+4 | $^{13}C_{12}{}^{35}Cl_7{}^{37}Cl_3$ | Deca-13C |

1. Nuclidic masses used: H = 1.007825 C = 12.00000 $^{13}C$ = 13.003355 F = 18.9984
O = 15.994915 $^{35}Cl$ = 34.968853 $^{37}Cl$ = 36.965903

Table 9

Theoretical Ion Abundance Ratios and Their Control Limits for PCBs

| Chlorine Atoms | m/z's Forming Ratios | Theoretical Ratio | Lower QC Limit | Upper QC Limit |
|---|---|---|---|---|
| 1 | m/m+2 | 3.13 | 2.66 | 3.60 |
| 2 | m/m+2 | 1.56 | 1.33 | 1.79 |
| 3 | m/m+2 | 1.04 | 0.88 | 1.20 |
| 4 | m/m+2 | 0.77 | 0.65 | 0.89 |
| 5 | m+2/m+4 | 1.55 | 1.32 | 1.78 |
| 6 | m+2/m+4 | 1.24 | 1.05 | 1.43 |
| 7 | m+2/m+4 | 1.05 | 0.89 | 1.21 |
| 8 | m+2/m+4 | 0.89 | 0.76 | 1.02 |
| 9 | m+2/m+4 | 0.77 | 0.65 | 0.89 |
| 10 | m+2/m+4 | 0.69 | 0.59 | 0.79 |

## Table 10 - Acceptance Criteria for Performance Tests

| Toxic & LOC Congeners | IUPAC | Test Conc. (ng/mL)[1] | IPR | | OPR(LCS) | VER |
|---|---|---|---|---|---|---|
| | | | RSD (%) | X (%) | (%) | (%) |
| 2-chlorobiphenyl | 1 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 4-chlorobiphenyl | 3 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2'-dichlorobiphenyl | 4 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 4,4'-dichlorobiphenyl | 15 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',6-trichlorobiphenyl | 19 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 3,4,4'-trichlorobiphenyl | 37 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',6,6'-tetrachlorobiphenyl | 54 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 3,3',4,4'-tetrachlorobiphenyl | 77 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 3,4,4',5-tetrachlorobiphenyl | 81 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2'4,6,6'-pentachlorobiphenyl | 104 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3,3',4,4'-pentachlorobiphenyl | 105 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3,4,4',5-pentachlorobiphenyl | 114 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3',4,4',5-pentachlorobiphenyl | 118 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2',3',4,4',5-pentachlorobiphenyl | 123 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 3,3',4,4',5-pentachlorobiphenyl | 126 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',4,4',6,6'-hexachlorobiphenyl | 155 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3,3',4,4',5-hexachlorobiphenyl | 156 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3',4,4',5,5'-hexachlorobiphenyl | 157 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3,3',4,4',5'-hexachlorobiphenyl | 167 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 3,3',4,4',5,5'-hexachlorobiphenyl | 169 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',3,4'5,6,6'-heptachlorobiphenyl | 188 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3,3',4,4',5,5'-heptachlorobiphenyl | 189 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',3,3',5,5',6,6'-octachlorobiphenyl | 202 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,3,3',4,4',5,5',6-octachlorobiphenyl | 205 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl | 206 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl | 208 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl | 209 | 50 | 40 | 60-140 | 50-150 | 70-130 |
| **All other congeners** | | 50 | NA | NA | NA | 70-130[2],40-160[3] |
| **Labeled Internal Standards** | | | | | | |
| $^{13}C_{12}$-2-chlorobiphenyl | 1L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-4-chlorobiphenyl | 3L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2'-dichlorobiphenyl | 4L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-4,4'-dichlorobiphenyl | 15L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',6-trichlorobiphenyl | 19L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-3,4,4'-trichlorobiphenyl | 37L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl | 54L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl | 77L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl | 81L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl | 104L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl | 105L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl - | 114L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl | 118L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl | 123L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl | 126L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl | 155L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl | 156L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl | 157L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl | 167L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl | 169L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl | 170L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl | 188L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl | 189L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl | 202L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl | 205L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl | 206L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl | 208L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| $^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl | 209L | 100 | 50 | 35-135 | 30-140 | 50-150 |
| **Cleanup standards** | | | | | | |
| $^{13}C_{12}$-2,4,4'-trichlorobiphenyl | 28L | 50 | 45 | 45-120 | 40-125 | 60-130 |
| $^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl | 111L | 50 | 45 | 45-120 | 40-125 | 60-130 |
| $^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl | 178L | 50 | 45 | 45-120 | 40-125 | 60-130 |
| **Labeled Surrogate Standards** | | | | | | |
| $^{13}C_{12}$-2,4'-trichlorobiphenyl | 8L | 50 | NA | NA | 50-150[4] | 70-130 |
| $^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl | 79L | 50 | NA | NA | 50-150 | 70-130 |
| $^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl | 95L | 50 | NA | NA | 50-150 | 70-130 |
| $^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl | 153L | 50 | NA | NA | 50-150 | 70-130 |

1 Test concentrations are based on ng/mL in the sample extract or standard solution.
2 If the concentration is within 70-130% of the test concentration then the ICAL RF is used.
3 If the concentration is outside the 70-130% limit but within 40-160% of the test concentration then the VER daily RF is used.

Table 11

Retention Times of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[1,2]

**PCB Congener Mix 1 (Accustandard S-4687-A)[1]**

| Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 16:11 | 4 | 78 | 37:58 | 6 | 161 | 42:50 |
| 2 | 10 | 16:55 | 4 | 81 | 38:28 | 6 | 153 | 43:21 |
| 2 | 9 | 18:59 | 5 | 96 | 30:22 | 6 | 130 | 44:05 |
| 2 | 6 | 19:29 | 5 | 103 | 32:15 | 6 | 129 | 44:52 |
| 2 | 8 | 19:59 | 5 | 95 | 33:09 | 6 | 166 | 46:04 |
| 2 | 14 | 21:45 | 5 | 88 | 33:56 | 6 | 159 | 47:03 |
| 2 | 11 | 22:46 | 5 | 89 | 34:48 | 6 | 167 | 47:52 |
| 3 | 30 | 22:19 | 5 | 92 | 35:33 | 6 | 156 | 49:10 |
| 3 | 27 | 23:10 | 5 | 113 | 36:05 | 7 | 179 | 42:25 |
| 3 | 32 | 24:05 | 5 | 83 | 36:43 | 7 | 176 | 43:22 |
| 3 | 34 | 25:21 | 5 | 119 | 37:16 | 7 | 178 | 45:09 |
| 3 | 26 | 25:51 | 5 | 87 | 37:30 | 7 | 175 | 45:53 |
| 3 | 31 | 26:32 | 5 | 85 | 38:00 | 7 | 183 | 46:46 |
| 3 | 33 | 27:06 | 5 | 82 | 38:48 | 7 | 177 | 47:38 |
| 3 | 36 | 29:09 | 5 | 120 | 39:29 | 7 | 171 | 48:17 |
| 3 | 38 | 30:12 | 5 | 124 | 40:43 | 7 | 172 | 49:51 |
| 3 | 35 | 30:46 | 5 | 106 | 41:17 | 7 | 191 | 50:57 |
| 4 | 50 | 26:11 | 5 | 122 | 41:56 | 7 | 170 | 51:58 |
| 4 | 45 | 27:01 | 5 | 105 | 42:51 | 7 | 190 | 52:32 |
| 4 | 52 | 28:48 | 5 | 127 | 44:13 | 8 | 200/201 | 48:33 |
| 4 | 49 | 29:19 | 6 | 152 | 36:12 | 8 | 204 | 49:13 |
| 4 | 75 | 30:12 | 6 | 136 | 36:49 | 8 | 199/200 | 49:43 |
| 4 | 41 | 30:56 | 6 | 148 | 38:32 | 8 | 198 | 52:34 |
| 4 | 72 | 32:02 | 6 | 151 | 39:13 | 8 | 196 | 53:17 |
| 4 | 57 | 32:49 | 6 | 144 | 39:51 | 8 | 195 | 54:58 |
| 4 | 63 | 33:38 | 6 | 143 | 40:35 | 8 | 194 | 57:22 |
| 4 | 66 | 34:20 | 6 | 142 | 41:19 | 9 | 207 | 55:38 |
| 4 | 79 | 37:19 | 6 | 133 | 42:03 | | | |

**PCB Congener Mix 2 (Accustandard S-4687-B)[1]**

| Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT |
|---|---|---|---|---|---|---|---|---|
| 2 | 7 | 19:10 | 4 | 55 | 34:32 | 6 | 139 | 40:49 |
| 2 | 5 | 19:54 | 4 | 60 | 35:25 | 6 | 132 | 41:41 |
| 2 | 12 | 23:09 | 5 | 94 | 32:37 | 6 | 165 | 42:25 |
| 3 | 18 | 22:27 | 5 | 100 | 33:11 | 6 | 168 | 43:24 |
| 3 | 24 | 23:17 | 5 | 91 | 33:59 | 6 | 137 | 44:17 |
| 3 | 23 | 25:28 | 5 | 121 | 35:00 | 6 | 160 | 44:56 |
| 3 | 28 | 26:52 | 5 | 90 | 36:07 | 6 | 128 | 46:13 |
| 3 | 22 | 27:35 | 5 | 99 | 36:45 | 6 | 162 | 47:22 |
| 3 | 39 | 29:34 | 5 | 109/108 | 37:16 | 6 | 157 | 49:13 |
| 4 | 53 | 26:14 | 5 | 117 | 38:00 | 7 | 184 | 42:48 |
| 4 | 51 | 27:02 | 5 | 111 | 38:56 | 7 | 186 | 43:51 |
| 4 | 73 | 28:55 | 5 | 108/107 | 40:43 | 7 | 187 | 46:05 |
| 4 | 48 | 29:37 | 5 | 118 | 41:27 | 7 | 185 | 46:56 |
| 4 | 62 | 30:14 | 5 | 114 | 42:03 | 7 | 181 | 47:55 |
| 4 | 71 | 31:02 | 6 | 150 | 36:23 | 7 | 192 | 50:08 |
| 4 | 68 | 32:21 | 6 | 145 | 37:05 | 8 | 197 | 49:29 |
| 4 | 58 | 33:08 | 6 | 135 | 39:20 | 8 | 201/199 | 52:35 |
| 4 | 61 | 33:51 | 6 | 149 | 40:14 | 8 | 203 | 53:29 |

Table 11 Continued

Retention Times of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[1,2]

**PCB Congener Mix 3 (Accustandard S-4687-C)[1]**

| Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT |
|---|---|---|---|---|---|---|---|---|
| 2 | 13 | 23:10 | 4 | 80 | 35:36 | 6 | 140 | 40:51 |
| 3 | 17 | 22:53 | 5 | 93 | 33:18 | 6 | 146 | 42:42 |
| 3 | 29 | 25:51 | 5 | 84 | 34:22 | 6 | 141 | 43:41 |
| 3 | 20 | 26:54 | 5 | 101 | 36:12 | 6 | 164 | 44:30 |
| 4 | 46 | 27:22 | 5 | 112 | 36:54 | 6 | 158 | 45:09 |
| 4 | 65 | 29:52 | 5 | 86 | 37:25 | 7 | 182 | 46:21 |
| 4 | 59 | 30:17 | 5 | 116 | 38:06 | 7 | 174 | 47:05 |
| 4 | 40 | 31:02 | 5 | 107/109 | 40:58 | 7 | 173 | 48:14 |
| 4 | 67 | 33:16 | 6 | 154 | 39:24 | 7 | 193 | 50:32 |
| 4 | 76 | 33:58 | 6 | 147 | 40:16 | | | |

**PCB Congener Mix 4 (Accustandard S-4687-D)[1]**

| Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT |
|---|---|---|---|---|---|---|---|---|
| 3 | 25 | 26:08 | 4 | 64 | 31:17 | 5 | 123 | 41:06 |
| 3 | 21 | 27:01 | 4 | 70 | 33:58 | 6 | 134 | 40:32 |
| 4 | 69 | 29:14 | 5 | 102 | 33:26 | 6 | 131 | 41:08 |
| 4 | 47 | 29:56 | 5 | 97 | 37:25 | 6 | 163 | 44:47 |
| 4 | 42 | 30:31 | 5 | 115 | 38:22 | 7 | 180 | 50:33 |

**PCB Congener Mix 5 (Accustandard S-4687-E)[1]**

| Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT | Cl Level | BZ No.[3] | RT |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 13:46 | 4 | 74 | 34:00 | 6 | 169 | 52:38 |
| 1 | 3 | 16:23 | 4 | 56 | 35:07 | 7 | 188 | 41:58 |
| 2 | 4 | 16:47 | 4 | 77 | 39:07 | 7 | 189 | 55:11 |
| 2 | 15 | 23:33 | 5 | 104 | 29:53 | 8 | 202 | 47:35 |
| 3 | 19 | 20:23 | 5 | 98 | 33:29 | 8 | 205 | 57:52 |
| 3 | 16 | 23:28 | 5 | 125 | 37:25 | 9 | 208 | 54:35 |
| 3 | 37 | 31:18 | 5 | 110 | 38:23 | 9 | 206 | 59:43 |
| 4 | 54 | 23:55 | 5 | 126 | 46:02 | 10 | 209 | 1:01:22 |
| 4 | 43 | 29:06 | 6 | 155 | 35:48 | | | |
| 4 | 44 | 30:00 | 6 | 138 | 44:47 | | | |

Notes:

1 Accustandard products S-4687-A to S-4687-E have been replaced by Accustandard product M-1668A-1 to M-1668A-5.

2 Each congener mix is analyzed in triplicate to establish the retention times of the PCB isomers in the absence of co-eluting isomers. The elution order listed here is used to assign peak identifications in the separate mixture analysis. The average retention time established in the analysis of the separate mixtures is then used to establish relative retention times. ( See sections 10.2.3)

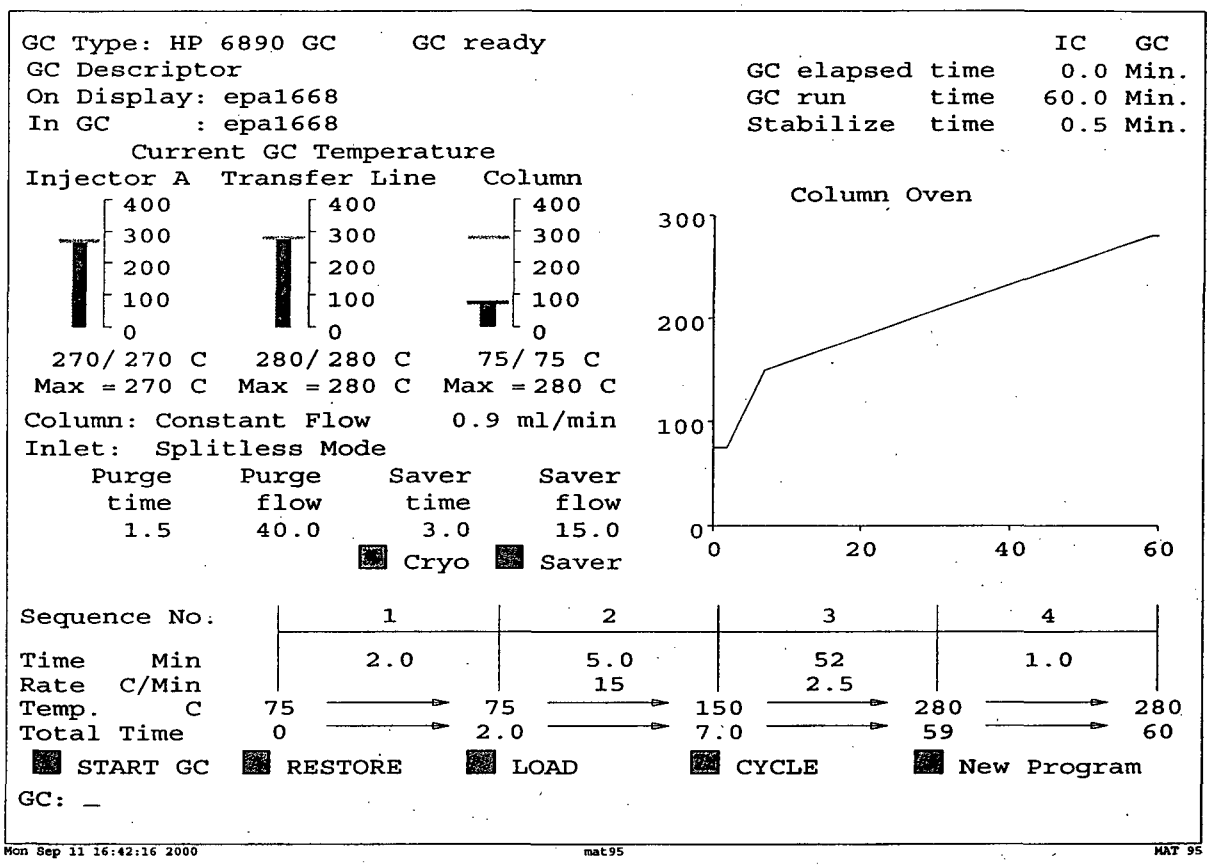
3 BZ/IUPAC Number, if different.

Table 12

| Assignment of Sample Preparation Protocols | | | | | | |
|---|---|---|---|---|---|---|
| With Associated Sample Weights, Volumes, and Concentration Factors | | | | | | |
| Estimated Concentration of Largest Congener Peak (4X Largest Congener Conc) (ng/g) | Protocol Number and Name | Sample Amount Extracted (g) | Volume of Spiking Solution Used (mL) | Extract Used (%) | Dilution Factor | EML & Calibration Range Multiplier |
| 0-9 | 1 – Default, Clean | 10 | 1 | 100 | 1 | 1 |
| 10-249 | 2 – Low Level | 10 | 1 | 100 | 5 | 5 |
| 250-1999 | 3 – Medium Level | 5 | 2 | 50 | 10 | 40 |
| 1999-10000 | 4- High Level | 2 | 4 | 25 | 10 | 200 |
| | | | | | | |

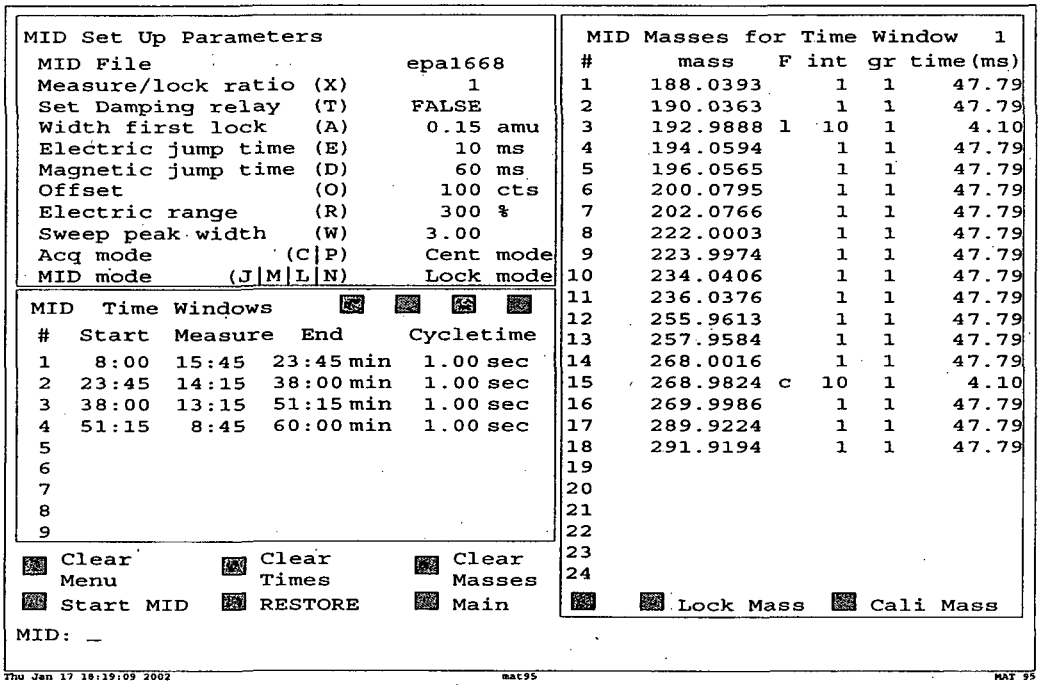
**Figure 1**

**Recommended GC Operating Conditions**

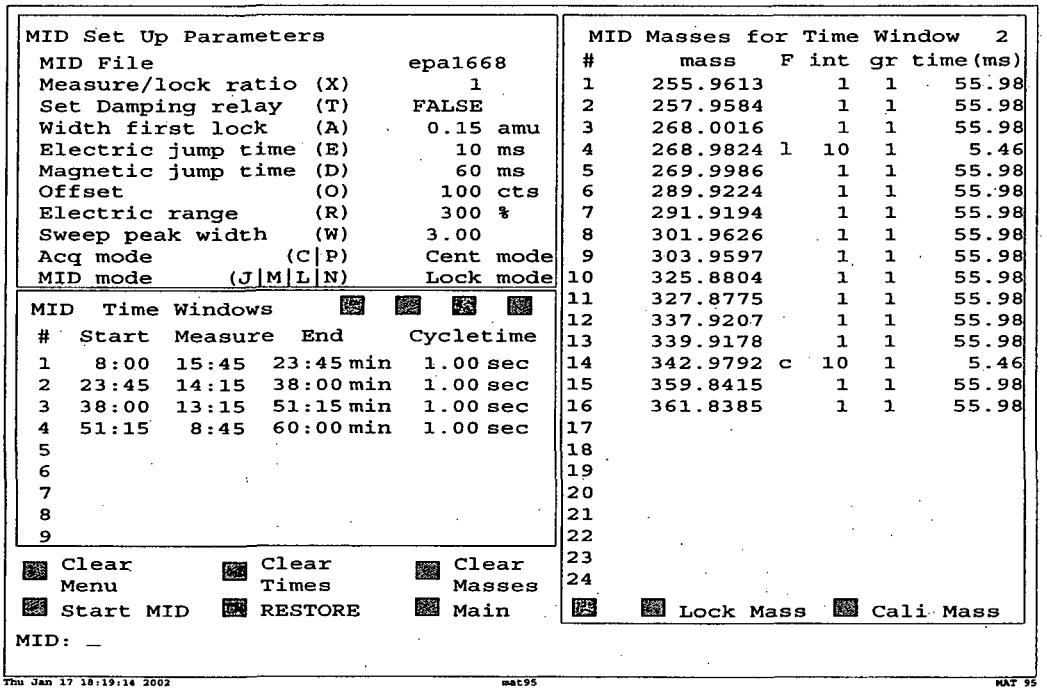


## Figure 2

## Recommended MID Descriptors



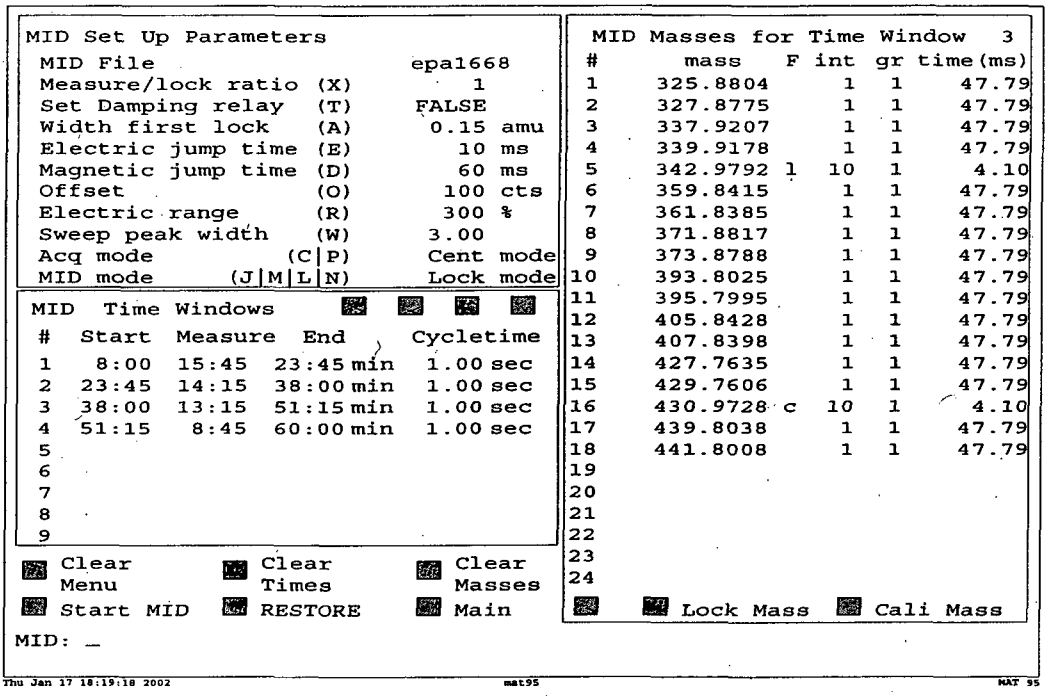
```
MID Set Up Parameters
 MID File                          epa1668
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)          0.15 amu
 Electric jump time  (E)            10 ms
 Magnetic jump time  (D)            60 ms
 Offset              (O)           100 cts
 Electric range      (R)           300 %
 Sweep peak width    (W)          3.00
 Acq mode          (C|P)          Cent mode
 MID mode       (J|M|L|N)         Lock mode

MID  Time Windows
 #   Start  Measure  End       Cycletime
 1    8:00   15:45   23:45 min   1.00 sec
 2   23:45   14:15   38:00 min   1.00 sec
 3   38:00   13:15   51:15 min   1.00 sec
 4   51:15    8:45   60:00 min   1.00 sec
 5
 6
 7
 8
 9

 Clear Menu     Clear Times     Clear Masses
 Start MID      RESTORE         Main

MID: _

MID Masses for Time Window  1
 #      mass    F int  gr time(ms)
 1   188.0393      1   1    47.79
 2   190.0363      1   1    47.79
 3   192.9888 l   10   1     4.10
 4   194.0594      1   1    47.79
 5   196.0565      1   1    47.79
 6   200.0795      1   1    47.79
 7   202.0766      1   1    47.79
 8   222.0003      1   1    47.79
 9   223.9974      1   1    47.79
10   234.0406      1   1    47.79
11   236.0376      1   1    47.79
12   255.9613      1   1    47.79
13   257.9584      1   1    47.79
14   268.0016      1   1    47.79
15   268.9824 c   10   1     4.10
16   269.9986      1   1    47.79
17   289.9224      1   1    47.79
18   291.9194      1   1    47.79
19
20
21
22
23
24
     Lock Mass     Cali Mass

Thu Jan 17 18:19:09 2002        mat95        MAT 95
```



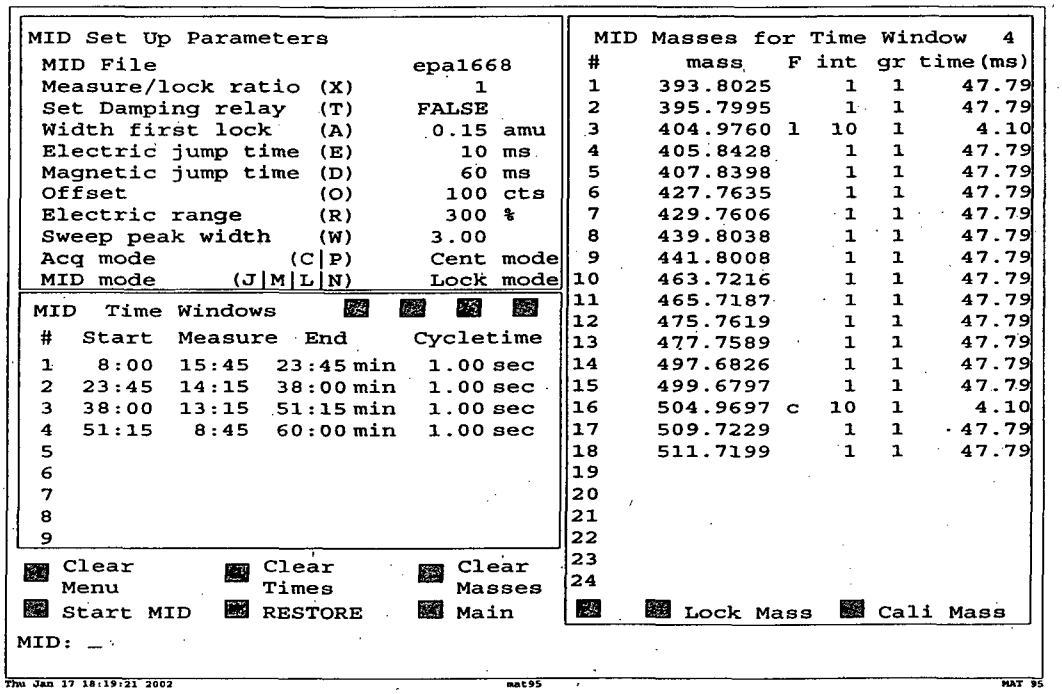
```
MID Set Up Parameters
 MID File                          epa1668
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)          0.15 amu
 Electric jump time  (E)            10 ms
 Magnetic jump time  (D)            60 ms
 Offset              (O)           100 cts
 Electric range      (R)           300 %
 Sweep peak width    (W)          3.00
 Acq mode          (C|P)          Cent mode
 MID mode       (J|M|L|N)         Lock mode

MID  Time Windows
 #   Start  Measure  End       Cycletime
 1    8:00   15:45   23:45 min   1.00 sec
 2   23:45   14:15   38:00 min   1.00 sec
 3   38:00   13:15   51:15 min   1.00 sec
 4   51:15    8:45   60:00 min   1.00 sec
 5
 6
 7
 8
 9

 Clear Menu     Clear Times     Clear Masses
 Start MID      RESTORE         Main

MID: _

MID Masses for Time Window  2
 #      mass    F int  gr time(ms)
 1   255.9613      1   1    55.98
 2   257.9584      1   1    55.98
 3   268.0016      1   1    55.98
 4   268.9824 l   10   1     5.46
 5   269.9986      1   1    55.98
 6   289.9224      1   1    55.98
 7   291.9194      1   1    55.98
 8   301.9626      1   1    55.98
 9   303.9597      1   1    55.98
10   325.8804      1   1    55.98
11   327.8775      1   1    55.98
12   337.9207      1   1    55.98
13   339.9178      1   1    55.98
14   342.9792 c   10   1     5.46
15   359.8415      1   1    55.98
16   361.8385      1   1    55.98
17
18
19
20
21
22
23
24
     Lock Mass     Cali Mass

Thu Jan 17 18:19:14 2002        mat95        MAT 95
```

## Figure 2 Continued

## Recommended MID Descriptors



```
MID Set Up Parameters
 MID File                          epa1668
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)           FALSE
 Width first lock    (A)          0.15 amu
 Electric jump time  (E)            10 ms
 Magnetic jump time  (D)            60 ms
 Offset              (O)           100 cts
 Electric range      (R)           300 %
 Sweep peak width    (W)          3.00
 Acq mode          (C|P)          Cent mode
 MID mode      (J|M|L|N)          Lock mode

MID  Time Windows
 #  Start  Measure  End       Cycletime
 1   8:00  15:45  23:45 min   1.00 sec
 2  23:45  14:15  38:00 min   1.00 sec
 3  38:00  13:15  51:15 min   1.00 sec
 4  51:15   8:45  60:00 min   1.00 sec
 5
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Start MID       RESTORE         Main

MID: _

MID Masses for Time Window   3
#       mass    F int gr time(ms)
1    325.8804      1  1    47.79
2    327.8775      1  1    47.79
3    337.9207      1  1    47.79
4    339.9178      1  1    47.79
5    342.9792 l   10  1     4.10
6    359.8415      1  1    47.79
7    361.8385      1  1    47.79
8    371.8817      1  1    47.79
9    373.8788      1  1    47.79
10   393.8025      1  1    47.79
11   395.7995      1  1    47.79
12   405.8428      1  1    47.79
13   407.8398      1  1    47.79
14   427.7635      1  1    47.79
15   429.7606      1  1    47.79
16   430.9728 c   10  1     4.10
17   439.8038      1  1    47.79
18   441.8008      1  1    47.79
19
20
21
22
23
24
   Lock Mass    Cali Mass

Thu Jan 17 18:19:18 2002   mat95   MAT 95
```



```
MID Set Up Parameters
 MID File                          epa1668
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)           FALSE
 Width first lock    (A)          0.15 amu
 Electric jump time  (E)            10 ms
 Magnetic jump time  (D)            60 ms
 Offset              (O)           100 cts
 Electric range      (R)           300 %
 Sweep peak width    (W)          3.00
 Acq mode          (C|P)          Cent mode
 MID mode      (J|M|L|N)          Lock mode

MID  Time Windows
 #  Start  Measure  End       Cycletime
 1   8:00  15:45  23:45 min   1.00 sec
 2  23:45  14:15  38:00 min   1.00 sec
 3  38:00  13:15  51:15 min   1.00 sec
 4  51:15   8:45  60:00 min   1.00 sec
 5
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Start MID       RESTORE         Main

MID: _

MID Masses for Time Window   4
#       mass    F int gr time(ms)
1    393.8025      1  1    47.79
2    395.7995      1  1    47.79
3    404.9760 l   10  1     4.10
4    405.8428      1  1    47.79
5    407.8398      1  1    47.79
6    427.7635      1  1    47.79
7    429.7606      1  1    47.79
8    439.8038      1  1    47.79
9    441.8008      1  1    47.79
10   463.7216      1  1    47.79
11   465.7187      1  1    47.79
12   475.7619      1  1    47.79
13   477.7589      1  1    47.79
14   497.6826      1  1    47.79
15   499.6797      1  1    47.79
16   504.9697 c   10  1     4.10
17   509.7229      1  1    47.79
18   511.7199      1  1    47.79
19
20
21
22
23
24
   Lock Mass    Cali Mass

Thu Jan 17 18:19:21 2002   mat95   MAT 95
```

Figure 3

## Example Data Review Checklist

**STL Knoxville Specialty Organics Group GC/MS Initial Calibration Data Review Checklist**
**Method or SOP Number: KNOX-ID-0013 Revision 4**

| PFK Date/Time: | | Inst: | | 2nd Source Filename: | |
|---|---|---|---|---|---|

| CS0.5 Filename | CS1 Filename | CS2 Filename | CS3 Filename | CS4 Filename | CS5 Filename |
|---|---|---|---|---|---|
| | | | | | |

| *Review Items* | N/A | Yes | No | If No, why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Was the mass resolution documented before beginning the initial calibration? | | | | | |
| 2. Was the instrument resolution ≥8,000 throughout and ≥ 10,000 in the center of each m/z range.<br>PFK m/z 192.9888, *230.9856, and *280.9824?<br>PFK m/z 268.9824, *292.9824, and *380.9760?<br>PFK m/z 342.9792, *380.9760, and *430.9728?<br>PFK m/z 404.9760, *442.9728, and *530.9665? | | | | | |
| 3. Were the measured exact masses listed above within 5 ppm at reduced accelerating voltage? | | | | | |
| 4. Have PCB Mixes 1 - 5 been analyzed in triplicate using the installed column to assign congener retention times, method retention times, and MID switchpoints? | | | | | |
| 5. Were the calibration standard solutions, at the number and concentrations specified in the Method/SOP, analyzed? | | | | | |
| 6. Was date/time of analysis verified between analysis header and logbook as correct? | | | | | |
| 7. Was the valley height less than 40% of the height of the shorter of the two peaks for the pair PCB 23 and PCB 34, and the pair PCB 182 and PCB 187 in the CS3 standard? | | | | | |
| 8. Was the absolute retention time of PCB 209 greater than 55 minutes in the CS3 standard? | | | | | |
| 9. Were the response factors calculated for each labeled standard and unlabeled native analyte using the Method/SOP specified reference compound, quantitation ions, and formula? | | | | | |
| 10. Is the %RSD acceptable for all native analytes (within ± 20% calculated by isotope dilution, within ± 35% calculated by internal standard)? | | | | | |
| 11. Is the %RSD acceptable (within ± 35%) for all labeled standards? | | | | | |
| 12. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards (Exception: Secondary native dichloro biphenyl channel m/z 223.9974)? | | | | | |
| 13. Are the ion abundance ratios in the CS 0.5 within the control limits specified? (Exception: native dichlorobiphenyls)? | | | | | |
| 14. Were all toxic congeners uniquely resolved from non-toxic congeners? | | | | | |
| 15. Was an ICV analyzed, calculated using the CS3 RRFs, and the %D within ± 35%)? | | | | □ < 5 outliers, none more than ±50% D. | |
| 16. If manual integrations were performed, are they clearly identified, initialed and dated? | | | | | |
| 17. If criteria were not met, was an NCM generated, approved by supervisor, and copy included in folder? | | | | | |
| 18. Does the ICAL folder contain complete data in the following order? Data review checklist, a complete runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard. | | | | | |

| Analyst: | Date: | 2nd Level Reviewer : | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

*At reduced accelerating voltage

Figure 3 **Continued**

## Example Data Review Checklist

**STL Knoxville Specialty Organics Group GC/MS Continuing Calibration Data Review Checklist**
**Method or SOP Number: KNOX-ID-0013 Revision 4**

| Start PFK: | | End PFK: | | CS3 Filename: | | Inst: | | ICAL Date: | |
|---|---|---|---|---|---|---|---|---|---|

| *Review Items* | N/A | Yes | No | If No, why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Was the mass resolution documented at both the beginning and end of the 12 hour shift? | | | | | |
| 2. Was the instrument resolution ≥8,000 throughout and ≥ 10,000 in the center of each m/z range.<br>PFK m/z 192.9888, *230.9856, and *280.9824?<br>PFK m/z 268.9824, *292.9824, and *380.9760?<br>PFK m/z 342.9792, *380.9760, and *430.9728?<br>PFK m/z 404.9760, *442.9728, and *530.9665? | | | | | |
| 3. Were the measured exact masses listed above within 5 ppm at reduced accelerating voltage? | | | | | |
| 4. Was date/time of analysis verified between analysis header and logbook as correct? | | | | | |
| 5. Were the MID switchpoints set to encompass the retention time windows of each congener group? | | | | | |
| 6. Was the valley height less than 40% of the height of the shorter of the two peaks for the pair PCB 23 and PCB 34, and the pair PCB 182 and PCB 187 | | | | | |
| 7. Was the continuing calibration performed at the beginning of the 12 hour period after successful mass resolution and GC resolution performance check? | | | | | |
| 8. Were the %D for all toxic analytes within ± 30%<br>(PCB 81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169, 189)<br>Were the %D for all LOC analytes within ± 30%<br>(PCB 1, 3, 4, 15, 19, 37, 54, 104, 155, 188, 202, 205, 206, 208, 209) | | | | | |
| 9. Were the %D for all non-toxic/non-LOC analytes within ± 30%? | | | | | |
| 10. If the %D for any non-toxic/non-LOC was not within ± 30, were response factors calculated from the continuing calibration for all non-toxic/non-LOC analytes with a %D greater than ± 30% but within ± 60%. | | | | | |
| 11. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula. | | | | | |
| 12. Were the absolute retention times of all labeled internal standards within ± 15 seconds of the retention times obtained during initial calibration? | | | | | |
| 13. Are %D within ± 50% for all labeled internal standards in the calibration? | | | | | |
| 14. Are the %D within ± 30% for all labeled surrogate standards in the calibration. | | | | | |
| 15. Are the %D within -40/+30% for all labeled cleanup standards in the calibration? | | | | | |
| 16. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards? | | | | | |
| 17. Are RRTs of all unlabled toxic/LOC analytes within their respective RRT limits? | | | | | |
| 18. If PCB 156 and 157 were classified as uniquely resolved in the most recent initial calibration, was the valley between the two less than or equal to the 50% of the height of the shorter of the two peaks? | | | | | |
| 19. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits? | | | | | |
| 20. If manual integrations were performed, are they clearly identified, initialed and dated? | | | | | |
| 21. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder? | | | | | |
| 22. Does the CCAL folder contain complete data in the following order? Data review checklist, a complete runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and both standards. | | | | | |

| Analyst: | Date: | 2nd Level Reviewer : | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

*At reduced accelerating voltage

## Figure 3 **Continued**

## Example Data Review Checklist

**STL Knoxville Specialty Organics Group GC/MS Data Review / Narrative Checklist LOT #_____**
**SOP Number: KNOX-ID-0013 Revision 4** **Page 1 of 2**

| Batch Number: | |
|---|---|

| *Review Items* A. Initial Calibration | N/A | Yes | No | Why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.) | | | | | |
| **B. Continuing Calibration** | | | | | |
| 1. Has a Continuing Calibration Checklist been completed for each analytical batch? | | | | | |
| **C. Client Sample AND QC Sample Results** | | | | | |
| 1. Were all special project requirements met? | | | | | |
| 2. Were the header information, prep factors, and dilution factors verified? | | | | | |
| 3. Was date/time of analysis verified between analysis header and logbook as correct? | | | | | |
| 4. Sample analyses done within preparation and analytical holding time (HT)?<br>*If no, list samples:* _____ | | | | ☐ HT expired upon receipt.<br>☐* Client requested analysis after HT expired.<br>☐ Re-extraction done after HT expired.<br>☐ See Comment no. | |
| 5. Are internal standards within QC limits?<br>*If no, list samples and reason (e.g., surl):*<br>Sample Reason Sample Reason<br>_____ _____ _____ _____<br>_____ _____ _____ _____<br>_____ _____ _____ _____<br>_____ _____ _____ _____<br>_____ _____ _____ _____<br>_____ _____ _____ _____<br>_____ _____ _____ _____ | | | | ☐* **[sup]** Ion suppression due to matrix.<br>☐* **[low]** Low recovery. S/N >10 and EDL<ML.<br>☐ **[sam]** Not enough sample to re-extract.<br>☐ **[dil]** Dilution showed acceptable %R.<br>☐ **[mtx]** Obvious matrix interference. Further cleanup not possible.<br>☐* **[unk]** At client's request, data was flagged as estimated and released without further investigation.<br>☐ **[com]** See Comment no. _____. | |
| 6. Were the following qualitative criteria met for all reported analytes:<br>• All analytes within Method/SOP retention time criteria and both ions maximized within ±2 seconds.<br>• The ion abundance ratios for all labeled and unlabeled analytes within the specified control limits.<br>• All peaks ≥2.5 S/N | | | | | |
| 7. Were peaks ≥2.5 S/N, which did not meet the above criteria, properly calculated and reported as EMPCs? | | | | | |
| 8. Are positive results within calibration range?<br>*If no, list samples:* _____ | | | | ☐ Sample extracted at lowest possible volume | |
| 11. If manual integrations were performed, are they clearly identified, initialed and dated? | | | | | |
| 12. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.) | | | | | |
| 13. Was a narrative prepared and all deviations noted? | | | | | |

* Such action must be taken in consultation with client.

## Figure 3 **Continued**

## Example Data Review Checklist

**STL Knoxville Specialty Organics Group GC/MS Data Review / Narrative Checklist LOT #_____**
**SOP Number: KNOX-ID-0013 Revision 4** **Page 2 of 2**

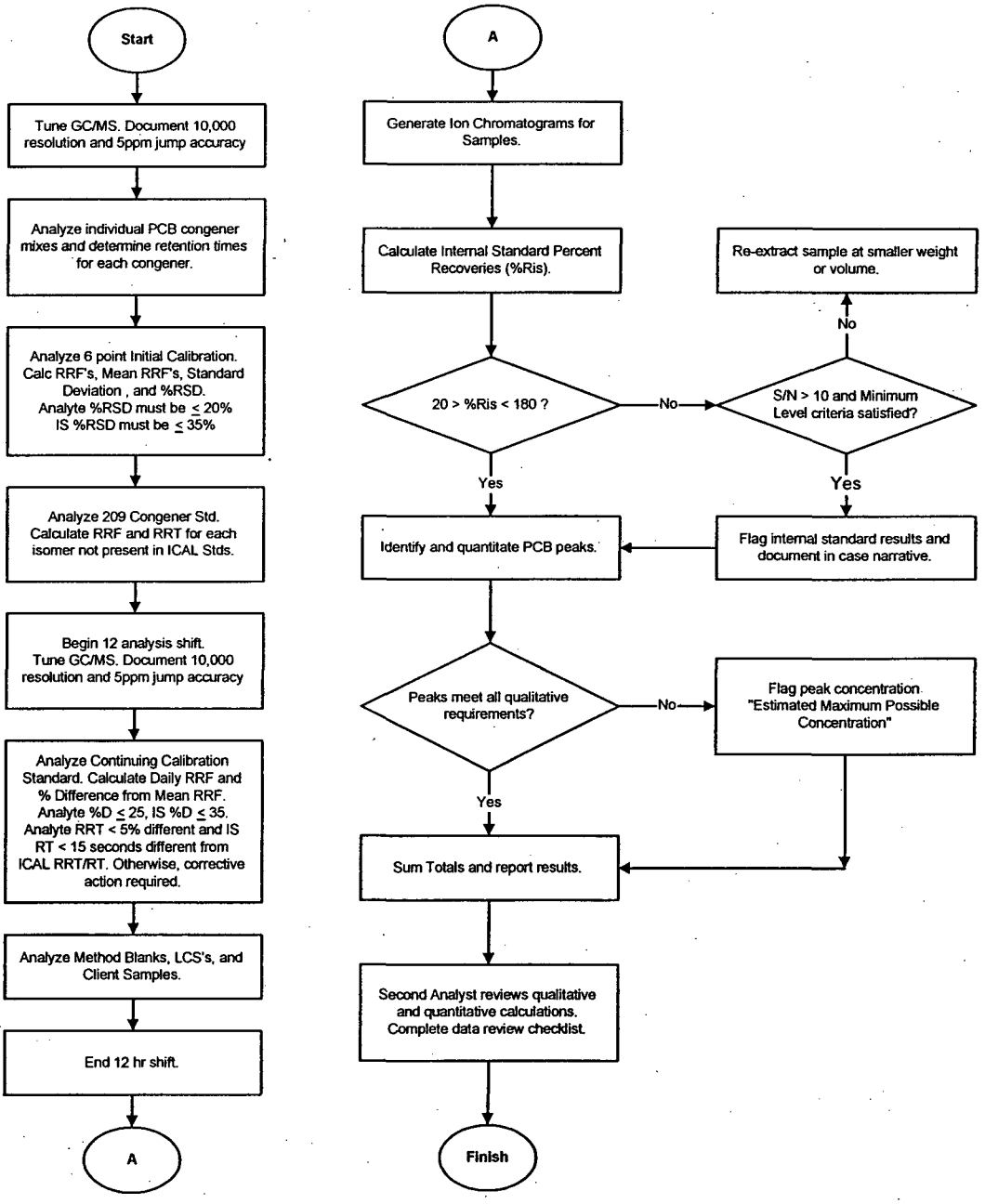
| D. Preparation/Matrix QC | N/A | Yes | No | Why is data reportable? | 2nd Level |
|---|---|---|---|---|---|
| 1. LCS done per prep batch and all analytes within laboratory established QC limits? *If no, list LCS ID:* _____ | | | | ☐ MS/MSD %R and all sample surrogate %R good indicating that problem was confined to the LCS. ☐* Reanalysis not possible-insufficient sample. ☐ LCS %R high and affected analyte(s) were <ML in associated samples. ☐ See Comment no. _____ | |
| 2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence? | | | | | |
| 3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____ | | | | ☐* Internal standards are high and blank demonstrates that analysis is free of contaminants. ☐* Sample internal standards OK and there is no analytes >ML in samples associated with blank. | |
| 4. Are all analytes present in the method blank ≤ EML? *If no, list blank ID:* _____ | | | | ☐ Sample results are > 20x higher than blank. ☐* There is no analyte > RL in the samples associated with method blank. ☐* Reanalysis not possible-insufficient sample | |
| 4. MS/MSD done per batch and are all recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD ID:* _____ | | | | ☐ LCS showed acceptable results indicating sample matrix effects. ☐ LCS showed acceptable results. High native analyte concentration relative to spike level. ☐ LCS showed acceptable results. RPD out due to lack of sample homogeneity. ☐ See Comment no. _____ | |
| E. Other | | | | | |
| 1. Are all nonconformances documented appropriately and copy included with deliverable? | | | | | |

| Analyst: | Date: | Analyst: | Date: |
|---|---|---|---|
| Comments: | | Comments: | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

* Such action must be taken in consultation with client.

## Figure 4

## Analysis of PCB's by HRGC/HRMS



# METHOD 200.7
# STANDARD OPERATING PROCEDURE
# FOR Trace Metals Analysis for Water and Wastewater Samples by Method 200.7 using Inductively Coupled Plasma Emission Spectroscopy

UNCONTROLLED COPY

**Approvals and Signatures**

| | | |
|---|---|---|
| Laboratory Director: | Christopher A. Ouellette | Date: 4/1/04 |
| Technical Director: | Michael J. Urban | Date: 4/1/04 |
| QA Manager: | Madhuri R. Dave | Date: 4/1/04 |
| Department Manager: | Chuangming Chen | Date: 3/31/04 |



## 1.0 SCOPE AND APPLICATION

1.1 Method 200.7 (40 CFR Part 136) determines trace elements in solution using inductively coupled plasma emission spectrometry (ICPES). The method is applicable to all of the elements listed in Table 1. All matrices require some type of digestion/preparation step prior to an analysis on the instrument.

1.2 Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Elements other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest is demonstrated.

Table 1

| Element | Element |
|---|---|
| Aluminum | Manganese |
| Antimony | Molybdenum |
| Arsenic | Nickel |
| Barium | Phosphorus |
| Beryllium | Potassium |
| Boron | Selenium |
| Cadmium | Silica (Si02) |
| Calcium | Silver |
| Chromium | Sodium |
| Cobalt | Strontium |
| Copper | Thallium |
| Iron | Tin |
| Lead | Titanium |
| Lithium | Vanadium |
| Magnesium | Zinc |

## 2.0 SUMMARY OF METHOD

2.1 A sample is digested and analyzed by Inductively Coupled Plasma. Each batch of no more than 20 samples, a matrix spike, blank and laboratory control sample is prepared and analyzed. The results are compared to laboratory control limits.

## 3.0 DEFINITIONS

3.1 Refer to document DEFDOC-04 for definitions.

## 4.0 INTERFERENCES

4.1. Most interferences are eliminated or greatly reduced during the acid digestion of the sample matrix.

4.2. Spectral interferences encountered on the instrument are corrected for by using baseline correction points and by applying background correction factors.

4.3. Background correction points are determined by scanning the area on either side of the wavelength and recording the apparent intensity from all other method

analytes. Use single element solutions at or near the upper linear range of each element.

4.4. Interelement Correction Factors are determined by analyzing single element solutions and recording the apparent analyte concentration.

4.5. All interfering elements must be analyzed at the same time as the elements of interest.

4.6. For sequential instruments the absence of spectral interference must be documented by scanning over a range of 0.5 nm centered on the wavelength.

4.7. Physical interferences are effects associated with sample nebulization and transport. They are reduced or eliminated with use of a peristaltic pump and internal standards. If these methods are insufficient to reduce the interference, they must be reduced by diluting the sample.

4.8. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. The necessary rinse times must be estimated prior to sample analysis. Until required rinse times are determined a suggested rinse time of 60 seconds shall be used. If a memory interference is suspected the sample must be reanalyzed.

4.9. High salt concentrations can cause analyte signal suppressions and confuse interference tests. Dilute the sample if necessary.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. The analyst must wear a protective lab coat, safety glasses, and gloves when handling all samples, standards and solvents.

5.3. All questions pertaining to any safety procedure should be brought to the department manager or STL Edison Safety Officer.

5.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Hydrochloric Acid | Corrosive Poison | 5 ppm-Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Nitric Acid | Corrosive Oxidizer Poison | 2 ppm-TWA 4 ppm-STEL | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| 1 - Always add acid to water to prevent violent reactions. | | | |
| 2 - Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Thermo Jarrel Ash Model 61E Trace ICP with 486 microprocessor, monitor, printer and autosampler. Resolution 0.011 nm on a holographically grooved grating (2400 grooves/mm). Vacuum purged spectrophotometer with a axial plasma torch.

6.2 TJA 61E ICP with 486 microprocessor, monitor, printer and autosampler. The optics consist of a 0.75 m Rowland circle with a Paschen-Runge mount. The spectrometer is nitrogen purged with a self-contained radio frequency generator.

6.3 Argon supply - 99.5% (Liquid)

6.4 Nitrogen supply - 99.5% (Liquid)

6.5 Operating conditions must be established by the analyst according to the

instrument manufacturer's specification and must meet conditions satisfying the analytical and quality assurance requirements. Table 1 lists these operating conditions. All data must be archived in a hard copy form for later reference.

## 7.0 REAGENTS AND STANDARDS

7.1 18 megohm Reagent grade Type II water

7.2 Concentrated distilled nitric acid--Trace Grade or Equivalent

7.3 Concentrated distilled hydrochloric acid--Trace Grade or Equivalent

7.4 Stock Solutions:

7.4.1 Calibration Standards – CLPP-CAL-1, CLPP-CAL-3, STLNJ-CAL-1A, STLNJ-CAL-1B , STLNJ-CAL-2, Aluminum, Zinc, and Lanthanum (Available from Inorganic Ventures, Lakewood, NJ.)

7.4.2 Calibration Verification Standards- QCP-CICV-1, QCP-CICV-3, STLNJ-QC-1A, STLNJ-QC-1B, STLNJ-QC-2, Aluminum, Zinc, and Lanthanum (Available from Inorganic Ventures Inc., Lakewood, NJ)

7.4.3 Interference Check Standards – CLPP-ICS-A, IV-7, IV-19, Sodium, Strontium, and Tin (Available from Inorganic Ventures Inc., Lakewood, NJ)

7.5 Working Solutions:

7.5.1 Working Calibration Standards

Calibration Standard One (CAL1): Add 1 ml each CLPP-CAL-1, CLPP-CAL-3, STLNJ-CAL-1A , and STLNJ-CAL-1B, 2ml of STLNJ-CAL-2, 2.3 ml of 10000 ppm Aluminum, 100 µl of 10000 ppm Zinc (TRACE 3) and 10 µl of 10000 ppm Lanthanum (TRACE 3) stock standard solutions to 1000 ml volumetric flask with 5% nitric acid. Record preparation in the ICP NON – CLP Standard Logbook.

Calibration Standard Two (CAL2): Add 5 ml each CLPP-CAL-1, CLPP-CAL-3, STLNJ-CAL-1A , and STLNJ-CAL-1B, 10 ml of STLNJ-CAL-2, 11.5 ml of 10000 ppm Aluminum, 500 µl of 10000 ppm Zinc (TRACE 3) and 50 µl of 10000 ppm Lanthanum (TRACE 3) stock standard solutions to 1000 ml volumetric flask with 5% nitric acid. Record preparation in the ICP NON – CLP Standard Logbook.

Calibration Standard Three (CAL3): Add 10 ml each CLPP-CAL-1,

CLPP-CAL-3, STLNJ-CAL-1A , and STLNJ-CAL-1B, 20ml of STLNJ-CAL-2, 23 ml of 10000 ppm Aluminum, 1 ml of 10000 ppm Zinc (TRACE 3) and 100 µl of 10000 ppm Lanthanum (TRACE 3) stock standard solutions to 1000 ml volumetric flask with 5% nitric acid. Record preparation in the ICP NON – CLP Standard Logbook.

7.5.2 Working Calibration Verification Standard (ICV/CCV):

Add 10 ml each QCP-CICV-1, QCP-CICV -3, STLNJ-QC-1A , and STLNJ-QC-1B, 20ml of STLNJ-QC-2, 11.5 ml of 10000 ppm Aluminum, 0.5 ml of 10000 ppm Zinc (TRACE 3) and 50 µl of 10000 ppm Lanthanum (TRACE 3) stock standard solutions to 1000 ml volumetric flask with 5% nitric acid. Record preparation in the ICP NON – CLP Standard Logbook.

7.5.3 Working Interference Check Standard A (ICSA)
Add 100 ml CLPP-ICS-A stock standard solution to 1000 ml volumetric flask with 5% nitric acid. Record preparation in the ICP NON – CLP Standard Logbook.

7.5.4 Working Interference Check Standard AB (ICSAB)
Add 100 ml CLPP-ICS-A, 1 ml each IV-7, IV-19, and LCSW-III, 0.9 ml each 10000 ppm Sodium and 10000 ppm Potassium standard solutions to 1000 ml volumetric flask with 5% nitric acid. Record preparation in the ICP NON – CLP Standard Logbook.

LCSW-III is one of the Laboratory control Sample mixed standards prepared in the laboratory. It contains 900 ppm Sodium, 100 ppm Tin and 100 ppm Strontium.

See Attachment A for the final concentrations of all the working standards.

## 8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Aqueous samples must be preserved with 2 mls of concentrated nitric acid to a pH of <2 at the time of collection.

Maximum holding time for the analysis of all metals except mercury is 180 days from the date of sampling. Maximum holding time for mercury is 28 days from the sampling date. Analysis of the samples must be completed during this time period in order to maintain compliance under this method.

## 9.0 QUALITY CONTROL

9.1 Instrument calibration should be verified in the following manner.

9.1.1 Analyze the highest mixed standard as if it were a sample. The results must be within 5% of the true value.

9.1.2 Instrument Check Standard (ICV/CCV) - Instrument calibration is verified using an independent standard after the high standard at the midpoint of the calibration curve different from the calibration standards. Results must be within 5% of the true value. Subsequent verification is performed after every 10 samples and at the end of the run using the same standard as above.

9.1.3 The results of the calibration blank analyzed after calibration must be less than the reporting limit.

9.1.4 The results of the check standard (CCV) are to agree within 5% of the true value. If not, terminate the analysis, correct the problem and recalibrate the instrument, and reanalyze the last 10 samples.

9.1.5 The absolute value of the calibration verification blank must not exceed the reporting limit. If it does, terminate the analysis, correct the problem, recalibrate and reanalyze the last 10 samples. The calibration verification blank is the same blank solution as used for initial calibration.

9.1.6 The interelement background correction factors are verified at the beginning and end of each run. This is done by analyzing the interferent solutions. Results should be within 20% of the true value for each solution.

9.2 One laboratory method/preparation blank will be analyzed with each batch of samples prepared at the same time (not to exceed 20 samples). Results must be less than detection limit.

If any analyte concentration in the blank is above this control limit, the batch must be prepared again for the element in question and the samples reanalyzed.

9.3 A Laboratory Control Sample (LCS) must be analyzed with each group of samples digested. For dissolved aqueous samples not undergoing a preparation procedure, the CCV may serve as the LCS. Results of the aqueous LCS must fall within ±20% of the true value. If not, all samples prepared in association with the LCS must be redigested and reanalyzed.

9.4 A blank spike and matrix spike are prepared and analyzed for each batch of samples. The sample is spiked at levels indicated in the standards logbook. The percent recovery is calculated using the following equation:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} \times 100$$

Where SSR = Spiked sample result
SR = Sample result
SA = Spike amount

A recovery of 75-125% is required. An exception to this occurs if the sample concentration exceeds the spike concentration by a factor of four or more. If the recovery is not within specified limits a post digestion spike is required to be analyzed at a concentration between 10 to 100 times the instrument detection limit. If the Post digestion spike recovery not recovered within 75-125% a matrix effect should be suspected. See above for the calculation.

9.5 A duplicate is analyzed for each batch of samples. The relative percent difference between the two results for the sample and the duplicate are determined by the following equation:

$$\text{RPD} = \frac{|S - D|}{(S + D)/2} \times 100$$

Where RPD = Relative Percent Difference
S = Original sample result
D = Duplicate sample result

The relative percent difference must fall within 20 % RPD for samples greater than ten times the detection limit.

9.6 A five fold serial dilution must be performed on one sample per batch. If the sample should contain analytes at a sufficiently high concentration; minimally a factor of 50 times above the instrumental detection limit, the results must agree within 10% of the original determination. If not, a chemical or physical effect should be suspected.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Profile and calibrate the instrument according to the instrument manufacturer's instructions using a high standard and a blank.

10.2 The instrument must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument is calibrated using three standards and a blank.

## 11.0 PROCEDURE

11.1 Instrument Operating Parameters

11.1.1 Set up the instrument with the operating parameters recommended by the manufacturer and as specified in the instrument operation SOPs.

11.1.2 Optimize the plasma operating conditions. This must only be done when the instrument is initially set up or when there is change in the instrument operating conditions. Follow instrument manufacturer instructions.

11.1.2.1 For the TJA 61E Trace ICP's use the following procedure:

11.1.2.1.1 After profiling using a 5 ppm arsenic standard. If the intensity is too low and/or the baseline is too high, optimize the nebulizer by adjusting the nebulizer position and changing the nebulizer pressure.

11.1.2.1.2 After optimizing the nebulizer align the torch by adjusting the adjustable screws that hold the optical path.

11.2 Instrument Performance Criteria

11.2.1 Prior to the analysis of any samples the following must be performed.

11.2.1.1 Background correction points must be determined during the initial set-up of the instrument. Refer to the specific instrument manual for instructions.

11.2.1.2 Interelement Correction factors must be determined annually. Refer to the instrument manufacturer recommended procedures and instrument operation SOP for instructions. Criteria for determining IEC's is an apparent positive or negative concentration for the analyte that falls within one reporting limit from zero.

11.2.1.3 The IDL for each analyte must be determined for each wavelength used on each instrument. The IDL must be determined semi-annually or if the instrument is adjusted in any way that may affect the IDL. The IDL is determined by multiplying by 3 the average of the standard deviations obtained from the analysis of seven replicates of a reagent blank signal.

11.2.1.4 The MDL must be determined on each instrument prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all elements of interest that have been carried through the entire analytical procedure. MDL's

must be redetermined yearly. The MDL may be analyzed on two or more non-consecutive days to provide a more appropriate estimate of the MDL. In this case calculate the MDL for each day and use an average of the values for each element.

11.2.1.5 Determine the linear dynamic range of the instrument by analyzing high standards at the upper limit of the instrument. The analytically determined concentration of this standard must be within 5% of the true value. The linear ranges should be redetermined every 6 months or if the instrument is significantly changed in any way.

11.2.1.6 Determine the calibration blank control limits by determining the standard deviation of the mean blank value of at least 20 calibration blanks. The control limit is two times the standard deviation. Note: The blank value may be in these control limits but above the element cleanup level needed. If this occurs reanalyze all associated samples.

11.3 Calibration

11.3.1 Profile and calibrate the instrument according to the instrument manufacturer's instructions using three standards and a blank.

11.3.2 The instrument must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument is calibrated using three standards and a blank. The correlation coefficient of the calibration curve must be ≥0.995. If it does not, the problem must be corrected, and the instrument must be recalibrated

11.4 Sample Analysis

11.4.1 Following a sample digestion procedure, the samples are ready for instrumental analysis. It is advisable to investigate each matrix for any complexities, which might adversely affect the acquisition of valid data. Flush the instrument between standards and sample using the calibration blank.

11.4.2 A minimum of two exposures for each standard, sample and blank is required. The average of the exposures is reported.

11.4.3 Any analyte exceeding the linear range must be diluted and reanalyzed.

11.4.4 All interfering elements must be analyzed at the same time as the elements of interest.

11.4.5 The following analytical run sequence is currently used for samples run under the SW846 6010B protocol:

Instrument Calibration(Blank and three standards)
IISA
ICV/CCV
ICB/CCB
ICSA
ICSAB
INT-20
7 Samples
CCV
CCB
10 Samples
CCV
CCB
Repeat until run is complete
CCV
CCB
ICSA
ICSAB
CCV
CCB

11.5 Full method required quality assurance data must be performed for each wavelength used.

11.6 All sample results must fall within the linear range. Dilute and reanalyze all samples for which the required analytes exceed the linear range as well as samples that contain high concentrations of an interfering element.

11.7 Data Processing Instrument calibration should be verified in the following manner.

11.7.1 Standard preparations must be documented in the Standard Preparation Logbook located in the metals analysis room.

11.7.2 See Operation SOP for documentation and reporting of data.

## 12.0 CALCULATIONS

12.1 Final Results for aqueous samples are as follows:

$$\text{Result (ug/L)} = \frac{A \times V1 \times D}{V2}$$

Where: A = Element concentration from instrument
D= Dilution performed on sample
V1= Final volume of sample digested (in liters)
V2= Initial volume of sample digested (in liters)

## 13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

## 14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. POLLUTION PREVENTION:

14.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When

wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

## 15.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated(flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

## 16.0 REFERENCES

16.140 CFR Part 136, App. C, Method 200.7

## 17.0 TABLES

## ATTACHMENT A: Working Standard Concentration for ICP Elements in ppb

| Element | CAL1 | CAL2 | CAL3 | ICV/CCV | ICSA | ICSAB |
|---|---|---|---|---|---|---|
| Aluminum | 25000 | 125000 | 250000 | 125000 | 500000 | 500000 |
| Antimony | 200 | 1000 | 2000 | 1000 | N/A | 100 |
| Arsenic | 1000 | 5000 | 10000 | 5000 | N/A | 100 |
| Barium | 2000 | 10000 | 20000 | 10000 | N/A | 100 |
| Beryllium | 200 | 1000 | 2000 | 1000 | N/A | 100 |
| Cadmium | 500 | 2500 | 5000 | 2500 | N/A | 100 |
| Calcium | 25000 | 125000 | 250000 | 125000 | 500000 | 500000 |
| Chromium | 1000 | 5000 | 10000 | 5000 | N/A | 100 |
| Cobalt | 500 | 2500 | 5000 | 2500 | N/A | 100 |
| Copper | 2500 | 12500 | 25000 | 12500 | N/A | 100 |
| Iron | 20000 | 100000 | 200000 | 100000 | 200000 | 200000 |
| Lead | 2000 | 10000 | 20000 | 10000 | N/A | 100 |
| Magnesium | 25000 | 125000 | 250000 | 125000 | 500000 | 500000 |
| Manganese | 1000 | 5000 | 10000 | 5000 | N/A | 100 |
| Nickel | 500 | 2500 | 5000 | 2500 | N/A | 100 |
| Potassium | * | * | 100000 | 50000 | N/A | 10000 |
| Selenium | 1000 | 5000 | 10000 | 5000 | N/A | 100 |
| Silver | 250 | 1250 | 2500 | 1250 | N/A | 100 |
| Sodium | * | * | 250000 | 125000 | N/A | 10000 |
| Thallium | 1000 | 5000 | 10000 | 5000 | N/A | 100 |
| Vanadium | 500 | 2500 | 5000 | 2500 | N/A | 100 |
| Zinc** | 500 | 2500 | 5000 | 2500 | N/A | 100 |
| Boron | 200 | 1000 | 2000 | 1000 | N/A | 100 |
| Molybdenum | 500 | 2500 | 5000 | 2500 | N/A | 100 |
| Tin | 200 | 1000 | 2000 | 1000 | N/A | 100 |
| Titanium | 2000 | 10000 | 20000 | 10000 | N/A | 100 |
| Strontium | 1000 | 5000 | 10000 | 5000 | N/A | 100 |
| Lanthanum*** | 100 | 500 | 1000 | 500 | N/A | 100 |

* Second order curve fit is used for Sodium and Potassium. A correlation coefficient must be 0.995 or better.

** For TRACE 3: CAL1 = 1500ppb, CAL2 = 7500ppb , CAL3 = 15000 ppb, and ICV/CCV = 7500ppb.

*** Lanthanum line is available in TRACE 3 only.

# METHOD 245.1
# STANDARD OPERATING PROCEDURE
# FOR Mercury Analysis for Water and Wastewater Samples by 245.1 using the Leeman Mercury Analyzer (Cold Vapor Technique)

UNCONTROLLED COPY

## Approvals and Signatures

| | | |
|---|---|---|
| Laboratory Director: | Christopher A. Ouellette | Date: 4/1/04 |
| Technical Director: | Michael J. Urban | Date: 4/1/04 |
| QA Manager: | Madhuri R. Dave | Date: 4/1/04 |
| Department Manager: | Chuangming Chen | Date: 3/31/04 |



## 1.0 SCOPE AND APPLICATION

1.1. EPA Method 245.1 is applicable to the determination of mercury in water matrices. Mercury may be found in water in both inorganic and organic forms. Organomercury compounds must first be broken down to respond to the cold vapor atomic absorption technique.

1.2. The typical detection limit using a 100 ml sample size is 0.2 ug/L Hg.

## 2.0 SUMMARY OF METHOD

2.1 A sample is digested and analyzed by Cold Vapor Atomic Absorption. Each batch of no more than twenty samples, a matrix spike, duplicate, blank and laboratory control sample is prepared and analyzed. The results are compared to laboratory control limits.

## 3.0 DEFINITIONS

3.1 Refer to document DEFDOC-04 for definitions.

## 4.0 INTERFERENCES

4.1 The addition of potassium persulfate during the digestion step can eliminate the possible interference from sulfide in the sample without affecting the recovery of inorganic mercury.

4.2 Copper may also be a potential interference although no effect has been observed for samples containing up to 10 mg/l total copper.

4.3 Samples that contain high levels of chloride have a potential to interfere due to a reaction that takes place during the oxidation step. During this step chloride is converted to free chlorine which absorbs light at 253.7 nm. The analyst must not allow the chlorine to be swept into the optical cell. The possibility of the chlorine interfering with the analysis can be minimized by using and excess of up to 25 ml hydroxylamine sulfate.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. The analyst must wear a protective lab coat, safety glasses, and gloves when handling all samples, standards and solvents.

5.3. All questions pertaining to any safety procedure should be brought to the department manager or STL Edison Safety Officer.

5.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

## 5.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Mercury (1,000 PPM in Reagent) | Oxidizer Corrosive Poison | 0.1 Mg/M3 Ceiling (Mercury Compounds) | Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage. |
| Sulfuric Acid | Corrosive Oxidizer Dehydrator Poison | 1 Mg/M3-TWA | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| Nitric Acid | Corrosive Oxidizer Poison | 2 ppm-TWA 4 ppm-STEL | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrochloric Acid | Corrosive Poison | 5 PPM-Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are |

| | | | |
|---|---|---|---|
| | | | irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Potassium Permanganate | Oxidizer | 5 Mg/M3 for Mn Compounds | Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent. |
| Potassium Persulfate | Oxidizer | None | Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis. |
| 1 Always add acid to water to prevent violent reactions. | | | |
| 2 Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Glassware/Equipment:

6.1.1 300 ml BOD bottles

6.1.2 100 ml graduated cylinder

6.1.3 Eppendorf Pipettes and tips in various sizes

6.1.4 100 ml volumetric flasks

6.1.5 15 ml sample cups

6.2 Leeman Laboratories Inc. PS200 Automated Hg Analyzer

6.3 Computer and Printer with Leeman PS200 software

6.4 Pump tubing:

6.4.1 Sample, viton, blue tab

6.4.2 Reductant, red tab

6.4.3 Drain, black tab

6.5 Drying Tube - located prior to the optical cell loosely packed with >20 mesh Magnesium Perchlorate.

6.6 Nitrogen supply - capable of producing 80 PSI.

6.7 Water bath - capable of holding a temperature of 95°C.

## 7.0 REAGENTS AND STANDARDS

7.1 Sulfuric acid - Concentrated (Trace Grade or Equivalent)

7.2 Nitric acid - Concentrated (Trace Grade or Equivalent)

7.3 Hydrochloric acid-Concentrated (Trace Grade or Equivalent)

7.4 Potassium Permanganate (ACS Grade)

7.5 Potassium Persulfate (ACS Grade)

7.6 Sodium Chloride (analytical reagent grade)

7.7 Hydroxylamine Hydrochloride (ACS Grade)

7.8 Stannous Chloride (ACS Grade)

7.9 Deionized water - 18 megohm minimum

7.10 Magnesium Perchlorate, Anhydrous >20 mesh

7.11 0.5N Sulfuric acid - Cautiously add 14.0 ml of concentrated $H_2SO_4$ to 1 liter of deionized water.

7.12 10% Hydrochloric Acid- Cautiously add 200 mls of concentrated HCl to a container and bring to final volume of 2 liters with deionized water.

7.13 Stannous chloride solution - Add 50 g of $SnCl_2$ to 500 ml 10% HCl solution.

7.14 Sodium chloride/Hydroxylamine Hydrochloride solution - Dissolve 120 g of NaCl and 120 g of hydroxylamine hydrochloride in deionized water and dilute to 1 liter using deionized water.

7.15 Potassium persulfate ($K_2S_2O_8$) - 5% solution w/v - Dissolve 50 g of $K_2S_2O_8$ in 1

liter of deionized water.

7.16 Potassium permanganate ($KMnO_4$) 5% solution w/v - Dissolve 100 g of $KMnO_4$ in deionized water and dilute to 2 liters using deionized water.

7.17 Stock Solutions:

7.17.1 Stock Mercury Calibration and Calibration Verification Standards - (1ml= .1mg Hg)- Purchase from two different vendors.

7.18 Working Mercury Solutions:

7.18.1 Calibration Standards:

7.18.1.1 Intermediate Calibration Standard (Cal-Intermediate): Dilute 1 ml of IIg calibration stock standard (1 ml = .1 mg Hg) solution to 100 ml with deionized water = 1 mg Hg/100 ml or 10 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.18.1.2 Working Calibration Standard (DCAL-INT): Dilute 1 ml of Cal-Intermediate solution to 100 ml with 0.15% $HNO_3$ = 10 ug Hg/100 ml = 0.1 ug IIg/ml. Record the preparation in the Mercury Standard Logbook.

7.18.2 Calibration Verification Standards:

7.18.2.1 Intermediate Calibration Verification Standard (CCV-Intermediate): Dilute 1 ml of IIg calibration stock standard (1 ml = 1 mg Hg) solution to 100 ml with deionized water = 1 mg Hg/100 ml or 10 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.18.2.2 Working Calibration Verification Standard (DCALV-INT): Dilute 1 ml of CCV-Intermediate solution to 100 ml with 0.15% $HNO_3$ = 10 ug Hg/100 ml = 0.1 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.19 Calibration Standard Preparation: Use 6 - 100 ml volumetric flasks to prepare the standards. Add small portion of deionized water to each flask. Working in increasing order, spike the appropriate flasks with 0.0, 0.1, 1.0, 2.0, 5.0, and 10.0 ml of working Solution DCAL-INT. Bring to final volume of 100 mls and mix thoroughly. The corresponding concentrations are 0.0ppb, 0.1ppb, 1.0ppb, 2.0ppb, 5.0ppb, and 10.0ppb mercury respectively.

7.20 Mercury Calibration Verification Standard Preparation: Use one 100ml volumetric flask. Add a small portion of deionized water to the flask and spike with 5 mls of DCALV-INT. Bring to final volume of 100 mls and mix thoroughly. The corresponding concentration is 5ppb.

## 8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

8.1 Water samples are acidified at the time of collection with nitric acid to a pH of 2 or lower.

8.2 Samples are to be analyzed within 28 calendar days of sampling date.

## 9.0 QUALITY CONTROL

9.1 Prior to the analysis of any samples the following must be performed:

9.1.1 The IDL for each analyte must be determined for each wavelength used on each instrument. The IDL must be determined semi-annually or if the instrument is adjusted in any way that may affect the IDL. The IDL is determined by multiplying by 3 the average of the standard deviations obtained from the analysis of seven reagent blanks.

9.1.2 The MDL must be determined on each instrument prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with mercury that have been carried through the entire analytical procedure. MDL's must be redetermined yearly.

9.2 Instrument Calibration should be verified in the following manner:

9.2.1 Initial calibration is verified immediately after calibration using an independent check standard (ICV/CCV) and blank (ICB/CCB) at a concentration near the mid-point of the calibration. The results must be within 10% of the true value. If not terminate the analysis, correct the problem and recalibrate the instrument.

9.2.2 Subsequent calibration verification is performed after every 10 samples and at the end of the run using a check. The validity of the calibration curve must be verified periodically during an analysis. A Continuing Calibration Verification (CCV) solution must be analyzed following every ten analytical sample analyses. Use a concentration of mercury at the midpoint of the calibration range but different from the calibration standards (5.0ppb). The value obtained for the CCV must not differ from

the true value by more than 20%. If it does, the problem must be corrected and the previous ten samples reanalyzed following the last good calibration verification. NOTE: For Non-CLP sample analyses the ICV and CCV are performed using the same solution.

9.2.3 Following each calibration verification, a calibration blank must be analyzed. The results of this analysis must fall below the required detection limit. If it does not, a laboratory source contamination should be suspected, the problem corrected, instrument recalibrated and the previous ten samples reanalyzed following the last good calibration verification blank.

9.3 A preparation blank must be run for each batch of samples digested. Use deionized water for the blank. Results must be less than method detection limit, 5% of the regulatory limit for that analyte or 5% of the measured concentration in the sample. If the result is greater, the entire batch of samples digested with the preparation blank must be redigested.

9.4 A Laboratory Control Sample (LCSW) must be analyzed with each group of samples digested. Results of the aqueous LCS must fall within ±20% of the true value. If not, all samples prepared in association with the LCS must be redigested and reanalyzed.

9.5 A matrix spike is prepared and analyzed for each batch of samples. A portion of sample is spiked with 0.1 ug of mercury (1ml of standard DCAL-INT). This is equivalent to 1.0 ppb Hg if a 100 ml portion of sample is digested.

9.5.1 The percent recovery is calculated using the following equation:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spiked sample result
SR = Sample result
SA = Spike amount

A recovery of 75-125% is required.

9.6 A spiked blank must be run for each batch of samples digested. A blank is spiked with 0.1 ug of mercury (1ml of standard DCAL-INT). This is equivalent to 1.0 ppb Hg if a 100 ml portion of sample is digested. Calculate the recovery as above.

9.7 A duplicate sample analysis is performed on the sample used for the matrix spike if sufficient volume of sample exists. If this is not the case, choose another sample for duplicate analysis.

9.7.1 The relative percent difference is calculated using the following equation:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where RPD = Relative Percent Difference
S = Original sample result
D = Duplicate sample result

## 10.0 CALIBRATION AND STANDARDIZATION

The instrument must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument is calibrated according to the manufacturer's specifications and must contain at least four standards and a blank. The laboratory currently uses five standards and a blank. The correlation coefficient of the calibration curve must be ≥0.995. If it does not, the problem must be corrected, and the instrument must be recalibrated. Standard preparations must be documented in the Standard Preparation Logbook located in the Mercury analysis room.

## 11.0 PROCEDURE

11.1 Digestion:

11.1.1 For total mercury determination, follow steps 11.1.3-11.1.9 to digest the samples.

11.1.2 For dissolved mercury determination, a portion of sample is filtered through an all glass filtering apparatus containing a 0.45 micron filter before acidification with nitric acid to pH < 2. This procedure is usually performed in the field.

11.1.3 Prepare the calibration standards and Calibration Verification Standards as stated in section 7.19 and 7.20.

11.1.4 Transfer 100 ml sample (DI water for PBW, BSW and LCSW) or standard, or an aliquot diluted to 100ml, to an appropriately identified 300 ml BOD bottle. For QA samples, transfer 3 aliquots of 100 ml sample to four BOD battles labeled as SAMPLE, DUP and MS. Spike the LCSW

with 0.5 µg of mercury (5 ml of DCALV-INT standard), and spike BSW and MS with 0.1 µg of mercury (1 ml of DCAL-INT standard).

11.1.5 Add 5 ml concentrated $H_2SO_4$ and 2.5 ml concentrated $HNO_3$ mixing well after each addition.

11.1.6 Add 15 ml of potassium permanganate solution to each bottle. Mix well and let stand for 15 minutes (minimum); if the color has disappeared, add additional $KMnO_4$ until the purple color persists for at least 15 minutes (Note any amount of additional $KMnO_4$ in the sample preparation log). The same amount of $KMnO_4$ must be added to standards as is added to samples.

11.1.7 Add 8 ml potassium persulfate solution to each bottle.

11.1.8 Heat for 2 hours in a 95° C water bath. Remove from bath and cool.

11.1.9 Add 6 ml sodium chloride - hydroxylamine hydrochloride solution to reduce the excess permanganate. Mix well - solution should become colorless. If necessary additional sodium chloride - hydroxylamine HCl solution may be added. Wait at least 30 seconds after decolorization before analyzing.

11.2 Analysis:

11.2.5 Powering the Instrument:

11.2.5.1 Turn on Computer, Printer and Monitor.

11.2.5.2 Turn power on the PS200 Analyzer by pushing in the green button and the blue button along side to turn on the Hg lamp.

11.2.5.3 At C:\ICP> prompt, type PS and press enter (This will execute startup and the PS200 main menu will appear on the screen.

11.2.6 Plumbing the Reagent Lines:

11.2.6.1 One at a time, feed each of the pump tubes into a pump cassette, sliding the tube through the plastic clips at the bottom until the plastic tab is secure. Then, holding the tube taut, slide the loaded cassette onto the pump head and click the clamp, lever up. The tab end of the tube should be located at the front of the pump

head.

11.2.6.1.1 Reductant (Red); Connect tab end of tube to the reductant bottle and the other end to the bottom of the mixing tee.

11.2.6.1.2 Sample (Blue); Connect tab end of tube to the autosampler probe and the other end to the top of the mixing tee.

11.2.6.1.3 Drain (Black) Connect the tab end of tube to the sample discharge tube connected on the Liquid/Gas separator and the other end to the waste line.

11.2.7 Preparation of Reagents and Drying Tube:

11.2.7.1 Pour the $SnCl_2$ solution into the reductant bottle and connect to the red reductant tube connector.

11.2.7.2 Pour the ten percent HCl solution into the autosampler reservoir and submerge the autosampler arm.

11.2.7.3 Prepare the drying tube by plugging one end of the drying tube with quartz wool and filling with magnesium perchlorate. Plug the other end of the tube with quartz wool and connect to the gray drying tube fittings. Note: Do not pack tightly; the carrier gas with mercury vapor must flow freely through the quartz wool and magnesium perchlorate.

11.2.8 Start up of Instrument:

11.2.8.1 At the PS200 Main Menu Screen, press the Macro (F2) key on the keyboard.

11.2.8.2 Type WARMSTRT and press enter and turn on lamp. The system will wait for several minutes and turn on the pump and the gas. The message Warming Up will appear on the screen. This procedure will take approximately thirty minutes. Alternately turn on the instrument by stopping the overnite mode, and wait approximately thirty minutes for the instrument to be warmed up.

11.2.8.3 When the system is stable, a beep will sound and a System Ready message will appear on the screen. The PS200 is now ready

for operation.

11.2.9 Setting the Optics (Performing the Aperture Test):

11.2.9.1 Select the following options in sequence from the PS200 main menu: (U)tility,dia(G)nostics. Using the arrow keys scroll down to aperture test and then press enter.

11.2.9.2 An aperture reading will now appear on the screen. If the value is outside +/- 100, the aperture must be adjusted.

11.2.9.3 Expose the aperture adjustment screws by removing the front panel of the PS200. The panel is easily detached by pushing it up and pulling out.

11.2.9.4 Back-out (unscrew) the aperture screw which is threaded in the furthest with an Allen wrench and then press enter. Look at the aperture reading again on the screen. Repeat this until the value stops changing (this indicates that neither aperture is blocking the light path).

11.2.9.5 Turn the appropriate aperture screw in or clockwise 1/8th revolution (top aperture screw if the value is positive, bottom aperture screw if the value is negative) and press enter. **(Note: On a daily basis you will only need to use the bottom screw. The top screw should only need to be adjusted after major instrument maintenance.)**

11.2.9.6 Check the aperture reading and repeat this process until the reading is within +\- 100. Note: The ideal reading is zero.

11.2.10 Retrieving the Method/Data File:

11.2.10.1 Select the following options in sequence from the PS200 main menu, (P)rotocol and (G)et.

11.2.10.2 Type in the appropriate method and press enter.

11.2.10.3 The system will then prompt you for a folder name, which is the data storage file. Type in a data storage file and press enter. A prompt will then say folder _____ does not exist. Create (Y or N)? Type Y and press enter. (Note: The data storage file name is the batch number with HG and the run number. EG 5700HG1.)

11.2.11 Autosampler/Rack Entry Setup:

11.2.11.1 Select the following options in sequence from the PS200 main menu, (A)utosampler and (R)ack entry. Type in an autosampler rack station name and press enter. At the prompt: rack _____ type does not exist. Create (Y or N)? Type Y and press enter. (Note: The rack number is usually selected as the batch number.)

11.2.11.2 Press the Insert key and type one sample name for each sequence under the ID column while pressing enter after each entry.

11.2.11.3 After every tenth sample or after all the samples are entered, type QC in the next sequence number under the Macro column. This will execute a macro to run the continuing calibration verification standard and the continuing calibration blank. NOTE: Do not enter a sample name under the ID column with the same sequence number as the QC macro or the sample will not be analyzed.

11.2.11.4 Each autosampler station rack has a total of forty four sequence numbers.

11.2.12 Analysis of Samples:

11.2.12.1 Select the following options in sequence, Menu(F1)and (S)etup.

11.2.12.2 Press "1" and enter the autosampler rack station name. The set-up screen for that rack will appear and a "Begin Cup:" prompt will be displayed at the bottom of the screen.

11.2.12.3 Enter the number of the first cup to be sampled and press enter.

11.2.12.4 An "End Cup:" prompt will now be displayed at the bottom of the screen. Enter the number of the last cup to be sampled and press enter. Be sure to include the QC macro as cup number.

11.2.12.5 Type (N) for name. The system will prompt you for the name of the first check sample "C1". Enter CCB and enter.

11.2.12.6 The system will then prompt you for the second check sample "C2". Enter "ACCV" and enter.

11.2.12.7 Then enter the third check sample name under "C3". Enter ICV/CCV and enter. Then return to the main menu.

11.2.12.8 Select Data Output by typing (D) at the main menu. Type (S) to specify report. Type (O) to open the current report specifications and type (CONC.) to choose to report to print in concentration during analysis.

11.2.12.9 Pour out the Standards and Samples according the rack layout shown on the setup page.

11.2.12.9.1 Calibration Standards: S1(0.0-ppb), S2(0.1ppb), S3(1.0ppb), S4(2.0ppb), S5(5.0ppb), S6(10.0ppb).

11.2.12.9.2 Calibration Verification Standards: C1(0.0ppb), C2(5.0ppb), C3(5.0 ppb).

11.2.12.9.3 Samples: Pour out the samples in their appropriate sequence space in the station rack.

11.2.12.10 Prior to starting the run check that the gas and pump are on and that there is fresh magnesium perchlorate in the drying tube. Recheck the aperture and adjust if necessary as described above.

11.2.12.11 Press the macro (F2) key, type in the method name and press "enter". A macro will begin and sequentially run the calibration, calibration verification standards and the samples.

11.2.13 Short-Term shutdown:

11.2.13.1 Press the macro(F2) key, type OVERNITE, and press enter.

11.2.13.2 Turn off power to the lamp.

11.2.13.3 In "overnite" mode, the pump and gas flow will turn on every few minutes, run for a few seconds, and then stop. This cycle exercises the tubes to avoid flat spots and fatigue, and the gas flow keeps the optical cell dry. Make certain that the drying tube has been loosely packed. If the drying tube is blocked, liquid may flow back into the optical cell; requiring disassembly and cleaning.

11.2.13.4 For long term shutdown check the PS200 Automated Mercury Analyzer.

11.2.14 The following analytical run sequence must be used for samples run under Method 245.1:

Instrument Calibration (Blank and 5 Standards)
AICV/ACCV1
ICB/CCB1
10 Samples
ACCV2
CCB2
10 Samples
ACCV3
CCB3
Repeat until run is complete
ACCV
CCB

11.3 Data Processing

11.3.5 Standard preparations must be documented in the Standard Preparation Logbook located in the metals analysis room.

**11.3.6** Sample preparation and all other necessary documentation must be filled out in the appropriately.

## 12 CALCULATIONS

**12.1** Final Results for aqueous samples are as follows:

$$\text{Result (ug/L)} = \frac{A \times V1 \times D}{V2}$$

Where: A= Element concentration from instrument
D= Dilution performed on sample
V1= Final volume of sample digested (in liters)
V2= Initial volume of sample digested (in liters)

## 13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

## 14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. POLLUTION PREVENTION:

14.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

## 15.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR

## UNACCEPTABLE DATA

15.1 Data that fails to meet minimum acceptance criteria will be annotated(flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

## 16.0 REFERENCES

16.1. Standard Method for the Examination of Water and Wastewater, 19th edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C., 1995.

16.2. Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

16.3. Methods for Chemical Analysis of Water and, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; 200 Series Methods.

16.4. Leeman PS200 Operating Manual

# METHOD 7470A
# STANDARD OPERATING PROCEDURE
## FOR Mercury Analysis for Water and Wastewater Samples by 7470A using the Leeman Mercury Analyzer (Cold Vapor Technique)

UNCONTROLLED COPY

**Approvals and Signatures**

| | | |
|---|---|---|
| Laboratory Director: | Christopher A. Ouellette | Date: 4/1/04 |
| Technical Director: | Michael J. Urban | Date: 4/1/04 |
| QA Manager: | Madhuri R. Dave | Date: 4/1/04 |
| Department Manager: | Chuangming Chen | Date: 3/31/04 |



## 1.0 SCOPE AND APPLICATION

1.1. SW846 Method 7470A is applicable to the determination of mercury in water matrices. Mercury may be found in water in both inorganic and organic forms. Organomercury compounds must first be broken down to respond to the cold vapor atomic absorption technique.

1.2. The typical detection limit using a 100 ml sample size is 0.2 ug/L Hg.

## 2.0 SUMMARY OF METHOD

2.1 A sample is digested and analyzed by Cold Vapor Atomic Absorption. Each batch of no more than twenty samples, a matrix spike, duplicate, blank and laboratory control sample is prepared and analyzed. The results are compared to laboratory control limits.

## 3.0 DEFINITIONS

3.1 Refer to document DEFDOC-04 for definitions.

## 4.0 INTERFERENCES

4.1 The addition of potassium persulfate during the digestion step can eliminate the possible interference from sulfide in the sample without affecting the recovery of inorganic mercury.

4.2 Copper may also be a potential interference although no effect has been observed for samples containing up to 10 mg/l total copper.

4.3 Samples that contain high levels of chloride have a potential to interfere due to a reaction that takes place during the oxidation step. During this step chloride is converted to free chlorine which absorbs light at 253.7 nm. The analyst must not allow the chlorine to be swept into the optical cell. The possibility of the chlorine interfering with the analysis can be minimized by using and excess of up to 25 ml hydroxylamine sulfate.

## 5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. The analyst must wear a protective lab coat, safety glasses, and gloves when handling all samples, standards and solvents.

5.3. All questions pertaining to any safety procedure should be brought to the department manager or STL Edison Safety Officer.

5.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

## 5.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Mercury (1,000 PPM in Reagent) | Oxidizer Corrosive Poison | 0.1 Mg/M3 Ceiling (Mercury Compounds) | Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage. |
| Sulfuric Acid | Corrosive Oxidizer Dehydrator Poison | 1 Mg/M3-TWA | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| Nitric Acid | Corrosive Oxidizer Poison | 2 ppm-TWA 4 ppm-STEL | Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Hydrochloric Acid | Corrosive Poison | 5 PPM-Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are |

| | | | |
|---|---|---|---|
| | | | irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Potassium Permanganate | Oxidizer | 5 Mg/M3 for Mn Compounds | Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent. |
| Potassium Persulfate | Oxidizer | None | Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis. |
| 1 - Always add acid to water to prevent violent reactions. | | | |
| 2 Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Glassware/Equipment:

6.1.1 300 ml BOD bottles

6.1.2 100 ml graduated cylinder

6.1.3 Eppendorf Pipettes and tips in various sizes

6.1.4 100 ml volumetric flasks

6.1.5 15 ml sample cups

6.2 Leeman Laboratories Inc. PS200 Automated Hg Analyzer

6.3 Computer and Printer with Leeman PS200 software

6.4 Pump tubing:

6.4.1 Sample, viton, blue tab

6.4.2 Reductant, red tab

6.4.3 Drain, black tab

6.5 Drying Tube - located prior to the optical cell loosely packed with >20 mesh Magnesium Perchlorate.

6.6 Nitrogen supply - capable of producing 80 PSI.

6.7 Water bath - capable of holding a temperature of 95°C.

## 7.0 REAGENTS AND STANDARDS

7.1 Sulfuric acid - Concentrated (Trace Grade or Equivalent)

7.2 Nitric acid - Concentrated (Trace Grade or Equivalent)

7.3 Hydrochloric acid-Concentrated (Trace Grade or Equivalent)

7.4 Potassium Permanganate (ACS Grade)

7.5 Potassium Persulfate (ACS Grade)

7.6 Sodium Chloride (analytical reagent grade)

7.7 Hydroxylamine Hydrochloride (ACS Grade)

7.8 Stannous Chloride (ACS Grade)

7.9 Deionized water - 18 megohm minimum

7.10 Magnesium Perchlorate, Anhydrous >20 mesh

7.11 0.5N Sulfuric acid - Cautiously add 14.0 ml of concentrated $H_2SO_4$ to 1 liter of deionized water.

7.12 10% Hydrochloric Acid- Cautiously add 200 mls of concentrated HCl to a container and bring to final volume of 2 liters with deionized water.

7.13 Stannous chloride solution - Add 50 g of $SnCl_2$ to 500 ml 10% HCl solution.

7.14 Sodium chloride/Hydroxylamine Hydrochloride solution - Dissolve 120 g of NaCl and 120 g of hydroxylamine hydrochloride in deionized water and dilute to 1 liter using deionized water.

7.15 Potassium persulfate ($K_2S_2O_8$) - 5% solution w/v - Dissolve 50 g of $K_2S_2O_8$ in 1 liter of deionized water.

7.16 Potassium permanganate ($KMnO_4$) 5% solution w/v - Dissolve 100 g of $KMnO_4$ in deionized water and dilute to 2 liters using deionized water.

7.17 Stock Solutions:

7.17.1 Stock Mercury Calibration and Calibration Verification Standards - (1ml= .1mg Hg)- Purchase from two different vendors.

7.18 Working Mercury Solutions:

7.18.1 Calibration Standards:

7.18.1.1 Intermediate Calibration Standard (Cal-Intermediate): Dilute 1 ml of Hg calibration stock standard (1 ml = .1 mg Hg) solution to 100 ml with deionized water = 1 mg Hg/100 ml or 10 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.18.1.2 Working Calibration Standard (DCAL-INT): Dilute 1 ml of Cal-Intermediate solution to 100 ml with 0.15% $HNO_3$ = 10 ug Hg/100 ml = 0.1 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.18.2 Calibration Verification Standards:

7.18.2.1 Intermediate Calibration Verification Standard (CCV-Intermediate): Dilute 1 ml of Hg calibration stock standard (1 ml = 1 mg Hg) solution to 100 ml with deionized water = 1 mg Hg/100 ml or 10 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.18.2.2 Working Calibration Verification Standard (DCALV-INT): Dilute 1 ml of CCV-Intermediate solution to 100 ml with 0.15% $HNO_3$ = 10 ug Hg/100 ml = 0.1 ug Hg/ml. Record the preparation in the Mercury Standard Logbook.

7.19 Calibration Standard Preparation: Use 6 - 100 ml volumetric flasks to prepare the standards. Add small portion of deionized water to each flask. Working in increasing order, spike the appropriate flasks with 0.0, 0.1, 1.0, 2.0, 5.0, and 10.0 ml of working Solution DCAL-INT. Bring to final volume of 100 mls and mix

thoroughly. The corresponding concentrations are 0.0ppb, 0.1ppb, 1.0ppb, 2.0ppb, 5.0ppb, and 10.0ppb mercury respectively.

7.20 Mercury Calibration Verification Standard Preparation: Use one 100ml volumetric flask. Add a small portion of deionized water to the flask and spike with 5 mls of DCALV-INT. Bring to final volume of 100 mls and mix thoroughly. The corresponding concentration is 5ppb.

## 8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

8.1 Water samples are acidified at the time of collection with nitric acid to a pH of 2 or lower.

8.2 Samples are to be analyzed within 28 calendar days of sampling date.

## 9.0 QUALITY CONTROL

9.1 Prior to the analysis of any samples the following must be performed:

9.1.1 The IDL for each analyte must be determined for each wavelength used on each instrument. The IDL must be determined semi-annually or if the instrument is adjusted in any way that may affect the IDL. The IDL is determined by multiplying by 3 the average of the standard deviations obtained from the analysis of seven reagent blanks.

9.1.2 The MDL must be determined on each instrument prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with mercury that have been carried through the entire analytical procedure. MDL's must be redetermined yearly.

9.2 Instrument Calibration should be verified in the following manner:

9.2.1 Initial calibration is verified immediately after calibration using an independent check standard (ICV/CCV) and blank (ICB/CCB) at a concentration near the mid-point of the calibration. The results must be within 10% of the true value. If not terminate the analysis, correct the problem and recalibrate the instrument.

9.2.2 Subsequent calibration verification is performed after every 10 samples and at the end of the run using a check. The validity of the calibration curve must be verified periodically during an analysis. A Continuing Calibration Verification (CCV) solution must be analyzed following every ten analytical sample analyses. Use a concentration of mercury at the

midpoint of the calibration range but different from the calibration standards (5.0ppb). The value obtained for the CCV must not differ from the true value by more than 20%. If it does, the problem must be corrected and the previous ten samples reanalyzed following the last good calibration verification. NOTE: For Non-CLP sample analyses the ICV and CCV are performed using the same solution.

9.2.3 Following each calibration verification a calibration blank must be analyzed. The results of this analysis must fall below the required detection limit. If it does not, a laboratory source contamination should be suspected, the problem corrected, instrument recalibrated and the previous ten samples reanalyzed following the last good calibration verification blank.

9.3 A preparation blank must be run for each batch of samples digested. Use deionized water for the blank. Results must be less than method detection limit, 5% of the regulatory limit for that analyte or 5% of the measured concentration in the sample. If the result is greater, the entire batch of samples digested with the preparation blank must be redigested.

9.4 A Laboratory Control Sample (LCSW) must be analyzed with each group of samples digested. Results of the aqueous LCS must fall within ±20% of the true value. If not, all samples prepared in association with the LCS must be redigested and reanalyzed.

9.5 A matrix spike is prepared and analyzed for each batch of samples. A portion of sample is spiked with 0.1 ug of mercury (1ml of Working Solution DCAL-INT). This is equivalent to 1.0 ppb ug if a 100 ml portion of sample is digested.

9.5.1 The percent recovery is calculated using the following equation:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spiked sample result
SR = Sample result
SA = Spike amount

A recovery of 75-125% is required.

9.6 A spiked blank must be run for each batch of samples digested. A blank is spiked with 0.1 ug of mercury (1ml of Working Solution DCAL-INT). This is equivalent

to 1.0 ppb Hg if a 100 ml portion of sample is digested. Calculate the recovery as above.

9.7 A duplicate sample analysis is performed on the sample used for the matrix spike if sufficient volume of sample exists. If this is not the case, choose another sample for duplicate analysis.

9.7.1 The relative percent difference is calculated using the following equation:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where RPD = Relative Percent Difference
S = Original sample result
D = Duplicate sample result

9.7.2 The relative percent difference must fall within 20 % RPD for samples greater than ten times the detection limit.

## 10.0 CALIBRATION AND STANDARDIZATION

The instrument must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument is calibrated according to the manufacturer's specifications and must contain at least four standards and a blank. The laboratory currently uses five standards and a blank. The correlation coefficient of the calibration curve must be ≥0.995. If it does not, the problem must be corrected, and the instrument must be recalibrated. Standard preparations must be documented in the Standard Preparation Logbook located in the Mercury analysis room.

## 11.0 PROCEDURE

11.1 Digestion:

11.1.1 For total mercury determination, follow steps 11.1.3-11.1.9 to digest the samples.

11.1.2 For dissolved mercury determination, a portion of sample is filtered through an all glass filtering apparatus containing a 0.45 micron filter before acidification with nitric acid to pH < 2. This procedure is usually performed in the field.

11.1.3 Prepare the calibration standards and Calibration Verification Standards as stated in section 7.19 and 7.20.

11.1.4 Transfer 100 ml sample (DI water for PBW, BSW and LCSW) or standard, or an aliquot diluted to 100ml, to an appropriately identified 300 ml BOD bottle. For QA samples, transfer 3 aliquots of 100 ml sample to four BOD battles labeled as SAMPLE, DUP, and MS. Spike the LCSW with 0.5 µg of mercury (5 ml of DCALV-INT standard), and spike BSW, and MS with 0.1 µg of mercury (1 ml of DCAL-INT standard).

11.1.5 Add 5 ml concentrated $H_2SO_4$ and 2.5 ml concentrated $HNO_3$ mixing well after each addition.

11.1.6 Add 15 ml of potassium permanganate solution to each bottle. Mix well and let stand for 15 minutes (minimum); if the color has disappeared, add additional $KMnO_4$ until the purple color persists for at least 15 minutes (Note any amount of additional $KMnO_4$ in the sample preparation log). The same amount of $KMnO_4$ must be added to standards as is added to samples

11.1.7 Add 8 ml potassium persulfate solution to each bottle.

11.1.8 Heat for 2 hours in a 95° C water bath. Remove from bath and cool.

11.1.9 Add 6 ml sodium chloride - hydroxylamine hydrochloride solution to reduce the excess permanganate. Mix well - solution should become colorless. If necessary additional sodium chloride - hydroxylamine HCl solution may be added. Wait at least 30 seconds after decolorization before analyzing.

11.2 Analysis:

11.2.1 Powering the Instrument:

11.2.1.1 Turn on Computer, Printer and Monitor.

11.2.1.2 Turn power on the PS200 Analyzer by pushing in the green button and the blue button along side to turn on the Hg lamp.

11.2.1.3 At C:\ICP> prompt, type PS and press enter (This will execute startup and the PS200 main menu will appear on the screen.

11.2.2 Plumbing the Reagent Lines:

11.2.2.1 One at a time, feed each of the pump tubes into a pump cassette, sliding the tube through the plastic clips at the bottom until the plastic tab is secure. Then, holding the tube taut, slide the loaded cassette onto the pump head and click the clamp, lever up. The tab end of the tube should be located at the front of the pump head.

11.2.2.1.1 Reductant (Red); Connect tab end of tube to the reductant bottle and the other end to the bottom of the mixing tee.

11.2.2.1.2 Sample (Blue); Connect tab end of tube to the autosampler probe and the other end to the top of the mixing tee.

11.2.2.1.3 Drain (Black) Connect the tab end of tube to the sample discharge tube connected on the Liquid/Gas separator and the other end to the waste line.

11.2.3 Preparation of Reagents and Drying Tube:

11.2.3.1 Pour the $SnCl_2$ solution into the reductant bottle and connect to the red reductant tube connector.

11.2.3.2 Pour the ten percent HCl solution into the autosampler reservoir and submerge the autosampler arm.

11.2.3.3 Prepare the drying tube by plugging one end of the drying tube with quartz wool and filling with magnesium perchlorate. Plug the other end of the tube with quartz wool and connect to the gray drying tube fittings. Note: Do not pack tightly; the carrier gas with mercury vapor must flow freely through the quartz wool and magnesium perchlorate.

11.2.4 Start up of Instrument:

11.2.4.1 At the PS200 Main Menu Screen, press the Macro (F2) key on the keyboard.

11.2.4.2 Type WARMSTRT and press enter and turn on lamp. The system will wait for several minutes and turn on the pump and the gas. The message Warming Up will appear on the screen. This

procedure will take approximately thirty minutes. Alternately turn on the instrument by stopping the overnite mode, and wait approximately thirty minutes for the instrument to be warmed up.

11.2.4.3 When the system is stable, a beep will sound and a System Ready message will appear on the screen. The PS200 is now ready for operation.

11.2.5 Setting the Optics (Performing the Aperture Test):

11.2.5.1 Select the following options in sequence from the PS200 main menu: (U)tility,dia(G)nostics. Using the arrow keys scroll down to aperture test and then press enter.

11.2.5.2 An aperture reading will now appear on the screen. If the value is outside +/- 100, the aperture must be adjusted.

11.2.5.3 Expose the aperture adjustment screws by removing the front panel of the PS200. The panel is easily detached by pushing it up and pulling out.

11.2.5.4 Back-out (unscrew) the aperture screw which is threaded in the furthest with an Allen wrench and then press enter. Look at the aperture reading again on the screen. Repeat this until the value stops changing (this indicates that neither aperture is blocking the light path).

11.2.5.5 Turn the appropriate aperture screw in or clockwise 1/8th revolution (top aperture screw if the value is positive, bottom aperture screw if the value is negative) and press enter. **(Note: On a daily basis you will only need to use the bottom screw. The top screw should only need to be adjusted after major instrument maintenance.)**

11.2.5.6 Check the aperture reading and repeat this process until the reading is within +\- 100. Note: The ideal reading is zero.

11.2.6 Retrieving the Method/Data File:

11.2.6.1 Select the following options in sequence from the PS200 main menu, (P)rotocol and (G)et.

11.2.6.2 Type in the appropriate method and press enter.

11.2.6.3 The system will then prompt you for a folder name, which is the data storage file. Type in a data storage file and press enter. A prompt will then say folder _____ does not exist. Create (Y or N)? Type Y and press enter. (Note: The data storage file name is the batch number with HG and the run number. EG 5700HG1.)

11.2.7 Autosampler/Rack Entry Setup:

11.2.7.1 Select the following options in sequence from the PS200 main menu, (A)utosampler and (R)ack entry. Type in an autosampler rack station name and press enter. At the prompt: rack _____ type does not exist. Create (Y or N)? Type Y and press enter. (Note: The rack number is usually selected as the batch number.)

11.2.7.2 Press the Insert key and type one sample name for each sequence under the ID column while pressing enter after each entry.

11.2.7.3 After every tenth sample or after all the samples are entered, type QC in the next sequence number under the Macro column. This will execute a macro to run the continuing calibration verification standard and the continuing calibration blank. NOTE: Do not enter a sample name under the ID column with the same sequence number as the QC macro or the sample will not be analyzed.

11.2.7.4 Each autosampler station rack has a total of forty four sequence numbers.

11.2.8 Analysis of Samples:

11.2.8.1 Select the following options in sequence, Menu(F1)and (S)etup.

11.2.8.2 Press "1" and enter the autosampler rack station name. The set-up screen for that rack will appear and a "Begin Cup:" prompt will be displayed at the bottom of the screen.

11.2.8.3 Enter the number of the first cup to be sampled and press enter.

11.2.8.4 An "End Cup:" prompt will now be displayed at the bottom of the screen. Enter the number of the last cup to be sampled and press enter. Be sure to include the QC macro as cup number.

11.2.8.5 Type (N) for name. The system will prompt you for the name of the first check sample "C1". Enter CCB and enter.

11.2.8.6 The system will then prompt you for the second check sample "C2". Enter "ACCV" and enter.

11.2.8.7 Then enter the third check sample name under "C3". Enter ICV/CCV and enter. Then return to the main menu.

11.2.8.8 Select Data Output by typing (D) at the main menu. Type (S) to specify report. Type (O) to open the current report specifications and type (CONC.) to choose to report to print in concentration during analysis.

11.2.8.9 Pour out the Standards and Samples according the rack layout shown on the setup page.

11.2.8.9.1 Calibration Standards: S1(0.0-ppb), S2(0.1ppb), S3(1.0ppb), S4(2.0ppb), S5(5.0ppb), S6(10.0ppb).

11.2.8.9.2 Calibration Verification Standards: C1(0.0ppb), C2(5.0ppb), C3(5.0 ppb).

11.2.8.9.3 Samples: Pour out the samples in their appropriate sequence space in the station rack.

11.2.8.10 Prior to starting the run check that the gas and pump are on and that there is fresh magnesium perchlorate in the drying tube. Recheck the aperture and adjust if necessary as described above.

11.2.8.11 Press the macro (F2) key, type in the method name and press "enter". A macro will begin and sequentially run the calibration, calibration verification standards and the samples.

11.2.9 Short-Term shutdown:

11.2.9.1 Press the macro(F2) key, type OVERNITE, and press enter.

11.2.9.2 Turn off power to the lamp.

11.2.9.3 In "overnite" mode, the pump and gas flow will turn on every few minutes, run for a few seconds, and then stop. This cycle exercises the tubes to avoid flat spots and fatigue, and the gas flow keeps the optical cell dry. Make certain that the drying tube has been loosely packed. If the drying tube is blocked, liquid may flow back into the optical cell; requiring disassembly and cleaning.

11.2.9.4 For long term shutdown check the PS200 Automated Mercury Analyzer.

11.2.10 The following analytical run sequence must be used for samples run under Method 7470A:

Instrument Calibration (Blank and 5 Standards)
AICV/ACCV1
ICB/CCB1
10 Samples
ACCV2
CCB2
10 Samples
ACCV3
CCB3
Repeat until run is complete
ACCV
CCB

11.3 Data Processing

11.3.1 Standard preparations must be documented in the Standard Preparation Logbook located in the metals analysis room.

**11.3.2** Sample preparation and all other necessary documentation must be filled out in the appropriately.

## 12.0 CALCULATIONS

**12.1** Final Results for aqueous samples are as follows:

$$\text{Result (ug/L)} = \frac{A \times V1 \times D}{V2}$$

Where: A= Element concentration from instrument
D= Dilution performed on sample

V1= Final volume of sample digested (in liters)
V2= Initial volume of sample digested (in liters)

## 13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

## 14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. POLLUTION PREVENTION:

14.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

## 15.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

15.1 Data that fails to meet minimum acceptance criteria will be annotated(flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

## 16.0 REFERENCES

16.1. Standard Method for the Examination of Water and Wastewater, 19th edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C., 1995.

16.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

16.3 Methods for Chemical Analysis of Water and, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; 200 Series Methods.

16.4 Leeman PS200 Operating Manual

| STL-Edison Standard Operating Procedure | Revision Date: 24 June 2004 |
|---|---|
| Title: CYANIDE, Analysis of Total Cyanides in Drinking Water-Automated | SOP Number: Cn335404M |
| Laboratory Director: _____ | Revision 2 |
| Technical Director: _____ | |
| QA Manager: _____ | Page 1 of 16 |
| Department Manager: _____ | |
| File Location: f:\qaqc\sops\nelac\nelac sops 2004\140watch\cyanide\cn335404m.doc | |

1. SCOPE AND APPLICATION

1.1. Method EPA 335.4 and QuikChem Method 10-204-00-1-A are described in this SOP. The SOP is applicable to drinking water samples requiring cyanide determination. The method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for total cyanide.

1.2. This method is applicable to drinking, ground, surface and saline waters.

1.3. The automated method has a detector that is sensitive to approximately to 0.005 mg CN-/L.

2. METHOD SUMMARY

2.1. Cyanide is extracted into a sodium hydroxide solution using the EASY-Dist distillation apparatus. Using an automated colorimetric measurement, the cyanide is quantitated. For each batch of twenty samples or less, a matrix spike, matrix spike duplicate, preparation blank, high standard (LCS-H) and low standard (LCS-L) are extracted and analyzed. The results are compared to laboratory limits.

3. INTERFERENCES:

3.1. Drinking Water samples typically do not contain many interferences.

3.2. Interferences are reduced or eliminated by using the distillation procedure. For sulfide interference:

3.2.1. Place a drop of the sample on lead acetate test paper (which has been pre-moistened with pH 4 acetate buffer solution) to detect the presence of sulfides. If sulfides are present (test strip turns black), the sample

volume required for the cyanide determination should be increased by 25 milliliters (ml).

3.2.2. The total volume of sample should be treated with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide.

3.2.3. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper.

3.2.4. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis.

NOTE: Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss of cyanide on the precipitated material.

3.3. Oxidizing agents such as chlorine decompose cyanide. To determine if oxidizing agents are present test a drop of sample with potassium iodine-starch paper. If a blue color appears that indicates the need for treatment. A few crystals of ascorbic acid should be added to the sample until a drop of sample produces no blue color on the indicator paper. Add an additional 0.6g of ascorbic acid for each liter of sample volume.

3.4. Nitrates and nitrites may give high biased results. During distillation they form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose to generate HCN.

3.4.1. Nitrate and nitrite interferences are eliminated by treatment with sulfamic acid just before distillation.

3.5. Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6. Fatty acids, detergents, surfactants may cause foaming during the distillation process, making the endpoint difficult to detect. If this occurs, a Dow Corning 544 can be added to prevent the foam from collecting in the condenser.

4. APPARATUS AND MATERIALS

4.1. EASY-Dist distillation apparatus

4.2. Vacuum pump

4.3. Analytical balance

4.4. Class A volumetric flasks and pipettors

4.5. Micro-porous boiling Chips

4.6. 120 ml snap seal sample cups

4.7. Size 24/40 clips

4.8. KI – Starch test paper

4.9. Lead-Acetate paper (pre-moistened with pH 4 acetate buffer solution)

4.10. Automated continuous–flow injection analysis equipment with the following:

4.10.1. Autosampler

4.10.2. Multichannel proportioning pump

4.10.3. Reaction manifold

4.10.4. Colorimetric detector

4.10.5. Data system

4.10.6. Heating Unit

5. REAGENTS

5.1 Deionized water-18 megohm reagent grade Type II water.

5.2 Standard 0.0192N Silver nitrate solution (1 ml = 1 mg CN). Prepared by weighing 3.2647 g of dried $AgNO_3$, dissolved in distilled water and dilute to 1000ml.

5.3 Rhodanine indicator - p-dimethyl-aminobenzalrhodanine

5.4 Dow Corning 544 anti foam agent.

5.5 Cadmium carbonate (powder) ACS reagent.

5.6 Acetate Buffer - Dissolve 82.0 gram of $NaC_2H_3O_2 \times 3H_2O$ in 100ml DI water. Add sufficient glacial acetic acid and adjust pH to 4.5 (approx. 100 ml).

5.7 Reagents for cyanide distillation.

5.7.1 0.25M NaOH. Dissolve 10.0 g NaOH into 1L. Dilute to mark and invert to mix(6 months).

5.7.2 Sulfamic Acid Solution (0.4N): Dissolve 40.0 g. $H_2NSO_3$ into 1000ml of deionized water.

5.7.3 Magnesium chloride solution (2.5M): Dissolve 510 gm of $MgCl_2 \cdot 6H_2O$ in 1 liter of deionized water.

5.7.4 1:1 $H_2SO_4$: Slowly pour 500 ml $H_2SO_4$ into 500 ml deionized water. (Caution! Solution is very hot.)

5.8 Reagents for automated colorimetric determination.

5.8.1 Pyridine-Barbituric acid Reagent: In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 ml DEIONIZED WATER, rinsing down the sides of the beaker to wet the barbituric. Add 75 ml pyridine ($C_5H_5N$) while stirring and mix until barbituric acid dissolves. Add 15 ml conc. HCl (12 M HCl) and mix. Transfer to a 1 L volumetric flask, dilute to mark and invert to mix. (Prepare weekly).

5.8.2 Chloramine-T: Dissolve 2.0g chloramine-T hydrate in 500 ml deionized water. Prepare fresh daily.

5.8.3 Phosphate buffer: In a 1 L volumetric flask, dissolve 194.0 g potassium phosphate, monobasic, anhydrous, ($KH_2PO_4$) in approximately 800 ml of DEIONIZED WATER. Dilute to mark and invert to mix. (1 month).

5.8.4 0.25 M NaOH (carrier) See section 5.7.1.

6 STANDARDS

6.1 Stock cyanide solution: Dissolve 2.51 gm of KCN and 2.0 gm of KOH in 900 ml of deionized water. Standardize the solution with 0.0192N silver nitrate solution monthly. Adjust the concentration so that 1 ml = 1 mg $CN^-$·Record the preparation in the reagent logbook. Record the results of the standardization in the Standardization Reagents Logbook.

6.2 Initial Calibration Verification Solution (ICV) – is made using the same reagents as above or purchased as a solution but from a different vendor.

6.3 Laboratory Control Sample (LCS): Prepare a 0.2 ppm solution of cyanide using the ICV solution in Section 6.2.

6.4 Standardization of the Stock Cyanide Solution prepared in section 6.1 of this Procedure.

6.4.1 Prepare a 0.0356N KOH solution (2 gms per 1 liter of deionized water).

6.4.2 Pipet 5 mls of the stock cyanide solution into a 125 Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator (5.3). Add an additional 50 mls of 0.25 N. NaOH solution prepared in Section 5.7.1.

6.4.3 Using the 10 ml micro buret, titrate the stock cyanide solution to an endpoint of canary yellow to a salmon hue and record the volume of silver nitrate solution used for the

titration. Titrate a blank using the same amount of alkali and water.

6.4.4 The volume of silver nitrate solution divided by the volume of stock cyanide solution titrated equals the concentration of the stock cyanide solution.

6.4.5 Adjust the concentration so that 1ml = 1mg CN.

7 PRESERVATION AND HANDLING

7.1 Samples are collected in plastic bottles.

7.2 The holding time for cyanide is 14 days from sample collection.

7.3 Samples must be preserved with 2ml of 10N sodium hydroxide solution upon sample collection to pH>12 and stored at 4 °C.

7.4 For sample homogenization refer to SOP Subspl04.

8 SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SAFETY CONCERNS OR REQUIREMENTS

Ensure cooling water is turned on to the distillation unit. Otherwise the samples may boil over and come into contact with the heating plates. Potassium Cyanide will give off Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

8.5 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Phosphoric Acid | Corrosive | 1 Mg/M3 TWA | Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage. |
| Sodium Hydroxide | Corrosive | 2 Mg/M3-Ceiling | Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness. |
| Pyridine | Flammable Irritant | 5 ppm-TWA | Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage. |
| Barbituric Acid | Irritant | Not established | Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest. |
| Hydrochloric Acid | Corrosive Poison | 5 ppm – Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |

| | | | |
|---|---|---|---|
| Potassium Hydroxide | Poison Corrosive Reactive | 2 $mg/m^3$ – Ceiling | Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness. |
| Potassium Cyanide | Poison Corrosive | 5 Mg/M3 TWA as CN | **This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage. |
| Sodium Cyanide | Poison Corrosive | 5 $mg/m^3$ TWA as CN (skin) | **This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage. |
| Silver Nitrate | Poison Corrosive Oxidizer | 0.01$mg/m^3$ (TWA) for silver metal dust and fume as Ag | Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

9 PROCEDURE

9.1 Each sample matrix must be spot tested for the presence of interfering ions.

9.1.1 Check for the presence of chlorine using KI-Starch paper. See section 3.3.

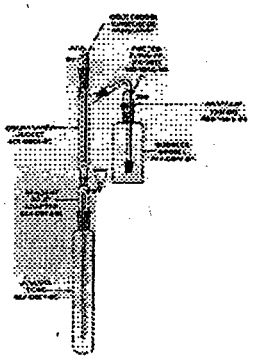
9.1.2 Check for the presence of sulfide using lead acetate paper (pre-moistened with pH4 acetate buffer solution). See section 3.2.1. - 3.2.4.

9.2 Distillation Procedure

9.2.1 Add 50 ml sample into the boiling tube. For solid samples, weigh 1.0 gram into the boiling tube and dilute to 50 ml with deionized water.

9.2.2 Add a few micro-porous boiling chips to the boiling tube.

**THE HEATER BLOCK TEMPERATURE MUST BE 70°C OR LOWER TO LOAD BOILING TUBES. DO NOT PRE-HEAT BLOCK ABOVE 70°C.** Loading tubes containing sample into a hot block will cause super-heating of samples and a potential boil-over of tube contents.



9.2.3 Add 50 mls of 0.25 M NaOH in bubbler vessel. Place the fritted bubbler (front) in the bubbler vessel and seal the joint with a size 24/40 clip. This is the NaOH absorber.

9.2.4 Connect the reagent inlet adapter to the boiling tube. Connect the cold finger jacket to the reagent inlet adapter. Attach the cold finger condenser to the cold finger jacket.

9.2.5 Attach the sealed NaOH absorber to the cold finger condenser. Turn the condenser water.

9.2.6 Put approximately 500 mls of NaOH in the excess cyanide trap.

9.2.7 Attach the black vacuum line from the EASY-Dist gas manifold port to the inlet of the NaOH absorber.

9.2.8 Turn vacuum on and adjust the individual air flow rate using the control knob at each manifold port. Adjust the flow such that **two to five bubbles per second** are exiting the base of the reagent inlet adapter. When properly adjusted, the NaOH absorber solution will be actively foaming without bubbling over into the vacuum line.

9.2.9 Add 5 mls sulfamic acid solution to the boiling tube through the reagent inlet adapter and **let mix for three minutes.**

9.2.10 Add 5 mls 1:1 $H_2SO_4$ to the boiling tube through the reagent inlet adapter. Rinse the acid down the inlet with *small volume of distilled water and* ***allow content to mix for three minutes.***

9.2.11 Add 2 mls magnesium chloride solution to the boiling tube through the reagent inlet adapter and rinse down with small volume of distilled water.

9.2.12 Turn on heating block. Heater block is set at 2.0 hour. Temperature should reach 125 +/- 3°C in approx. 20 minutes. The 1.5 hour reflux starts after the programmed temperature set point is reached. Heating block will automatically shut off after 1.5 hour.

9.3.13Periodically monitor the vacuum and heating to avoid excessive bubbling in the bubbler vessel. Adequate heating

is indicated by a constant reflux of condensed vapor off of the condenser. Discontinue heating but **maintain vacuum flow. Cool glassware apparatus for 15 minutes.**

9.3.14 Turn off vacuum pump. Remove bubbler vessel and transfer its contents into a 125ml snap seal cups. DO NOT DILUTE.

9.3.15 The solution is now ready for semi-automated colorimetry.

9.3.16Analyze on the LACHAT.

9.4 Preparation of Standards:

9.4.1. Use the 10 mg/l working standard to prepare calibration standards. Prepare 10 mg/l working standard by pipetting 1000ul of 1000 ppm CN- stock into 100 ml volumetric flask. Dilute to mark using 0.25 N NaOH. Use 0.25N NaOH to bring standards to volume. Prepare fresh daily.

| Volume of Spike Solution(ul) | Conc. CN- (mg/L) |
| --- | --- |
| 2000 | 0.40 |
| 1000 | 0.20 |
| 500 | 0.10 |
| 250 | 0.05 |
| 125 | 025 |
| 50 | 0.010 |
| 0 | 0.0 |

9.5 System startup:

9.5.1. Follow manifold scheme for this method.

9.5.2. Turn on heating unit at 60 °C for 15 minutes before analysis.

9.5.3. Put all reagent lines into deionized water and turn pump on. Check for leaks and slow flow rate.

9.5.4. Switch over reagent lines to proper reagent. Let reagent run through manifold for 15 minutes before analysis to allow baseline to stabilize.

9.6 Set up tray table with all appropriate QA checks. CCV/CCB every 10 samples and at the end of the run.

9.7 Place standards and samples into autosampler cups.

9.8 The following analytical run sequence must be used when analyzing samples for Method 335.4:
Instrument Calibration (Blank and 3 Standards)
IPC(CCV)
CCB
QCS(ICV)
10 Samples with Analytical Spikes
IPC(CCV)
CCB
Repeat until run is complete
IPC(CCV)
CCB

9.9 Run tray.

9.10 Correlation coefficient of 0.997 or greater must be obtained.

9.11 Calculate sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

9.12 Data Processing:

9.12.1. Record results in workbook. Report results in mg/L.

9.12.2. Place analyte sheets in job folders.

9.12.3. Notify supervisor if quality control limits are exceeded.

9.12.4. Submit quality control sheets as required for each batch.

10 QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed:

10.1.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water and process through the entire analytical method. MDLs should be determined yearly.

10.1.2. Linear Calibration Range (LCR) -- An LCR is determined daily. The curve correlation coefficient should be equal to or greater than 0.997.

10.2. Instrument calibration is verified in the following manner.

10.2.1. Quality Control Sample (ICV) -- An ICV is run daily to verify the calibration standards and acceptable instrument performance. The determined concentration must be within ± 10% of the values.

10.2.2. Instrument Performance Check (CCV and CCB) -- A calibration verification standard and a calibration blank immediately following daily calibration, after every 10th sample and at the end of the sample run must be analyzed. The analysis if the CCV verifies that the calibration is within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the CCV solution. If the second analysis of the CCV solution confirms calibration to be outside the limits, sample analysis must be discontinued. All samples following the last acceptable CCV solution must be reanalyzed. The analysis data of the calibration blank and CCV solution must be kept on file with the sample analysis data.

10.2.2.1. The calibration blank results must be less than the reporting limit.

10.3. Laboratory Reagent Blank (LRB) -- A Prep blank must be run with each setup of samples or every 20 samples whichever is less. Values that exceed the MDL indicate laboratory or reagent

contamination and corrective actions must be taken before continuing the analysis.

10.4. A low standard is distilled and analyzed each setup of samples using a 0.025 ppm standard. It's results must be compared to similar values on the calibration curve and must agree within 10%. Before distillation, standards should contain 4 ml. 0.25N NaOH per 50 ml.

10.5. Laboratory Fortified Sample Matrix (MS) -- Two portions of the sample (matrix spike and matrix spike duplicate) are spiked with 10 ug of cyanide. Laboratory acceptable MS/MSD recovery range is 90-110% or laboratory generated limits whichever is less provided limits were generated from more than 20 points.

10.5.1. If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related.

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to

minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

## 14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

## 15. REFERENCES

15.1 Methods for the Determination of Inorganic Substances in Environmental Samples, EMSL-Cincinnati, EPA/600/R-93/100, August 1993, Method - 335.4 Determination of Total Cyanide by Semi-Automated Colorimetry

15.2 QuikChem Method 10-204-00-1-A, Determination of Cyanide in Waters.

| STL Edison Standard Operating Procedure | Revision Date: April 1, 2004 |
|---|---|
| Title: NITRATE AND NITRITE MANUAL, Manual Colorimetric Analysis Of Nitrate And Nitrite | SOP Number NO32M04 |
| Laboratory Director: | Revision 2 |
| Technical Director: | Page 1 of 11 |
| QA Manager: | |
| Department Manager: | |
| File Location: t:\qaqc\sops\nelac\nelac sops 2004\t40wetch\nitrogen\no32m04.doc | |

UNCONTROLLED COPY

1. SCOPE AND APPLICATION

1.1. Methods EPA 353.3 and SM 4500 $NO_3$ E are described in this SOP. The SOP is applicable to waters and the leachates of soils. This method can be used to determine nitrate, nitrite, or both forms of nitrogen from 0.1-1.0 mg/l.

2. METHOD SUMMARY

2.1. Nitrate and nitrite are analyzed using a cadmium reduction column and subsequent manual colorimetric measurement for quantitation. Each batch of twenty samples or less, a laboratory control sample, matrix spike and matrix spike duplicate are analyzed. The results are compared to laboratory generated control limits. Each time samples are analyzed, an ICV, ICB and method blank are analyzed. The method blank and ICB must be less than the reporting limit. The ICV must recover between 90-110%.

2.2. Nitrate is reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water-soluble dye has a magenta color that is read at 540 nm. Nitrite alone can be determined by removing the cadmium column.

2.3. Determination of Nitrate - Analyze samples with and without elution through column. Subtract non-eluted sample from eluted sample.

2.4. Determination of Nitrite - Analyze samples without eluting through column.

2.5. Determination of Nitrate/Nitrite - Elute sample through cadmium reduction column.

3. INTERFERENCES

3.1. Filter samples if sample has particulates, color, or is turbid. Use a 0.45 um filter syringe.

4. APPARATUS AND MATERIALS

4.1. Photospectrometer, 540nm.

4.2. Reduction Column.

4.3. pH meter.

4.4. Specimen cups

4.5. Various pipettors or volumetric pipets

4.6. Volumetric flasks- various

4.7. 100 ml Graduated Cylinders

5. REAGENTS

5.1. Granulated cadmium, 40-60mesh.

5.2. Cu-Cd: Clean Cd Granules with 6N HCl and rinse with deionized water. Cd should appear silver, soak Cd granules in 2% copper sulfate solution until brown. Drain. Rinse granules in deionized water until rinse is clear of precipitate.

5.3. Hydrochloric Acid, 6N: Dilute 50ml conc. HCl to 100ml with deionized water. or 11 N Sulfuric Acid.

5.4. Ammonium hydroxide, conc. or 10 N Sodium Hydroxide

5.5. Buffer solution: Dissolve 13g ammonium chloride and 1.7g disodium ethylene diamine tetracetate in 900ml deionized water. Use pH meter and add conc. ammonium hydroxide to adjust pH=8.5. Prepare 1 liter of buffer for every analysis including standards. (CAUTION: PREPARE UNDER HOOD!)

5.6. Color Reagent: Dilute 100ml conc. phosphoric in 800ml deionized water. Dissolve 10g sulfanilamide and 1.0g N (1-naphthyl) ethylene diamine dihydrochloride. Dilute to 1 liter.

5.7. Copper Sulfate solution, 2%: Dissolve 20g $CuSo_4.5H_2O$ in deionized water and dilute to 1 liter.

6. STANDARDS

6.1. Stock Nitrate (1000mg/l): Dissolve 7.218g potassium nitrate in deionized water and dilute to 1.0liter. Preserve with 2ml chloroform per liter. Solution stable for 6 months.

6.2. Stock Nitrite (1000 mg/l): Dissolve 6.072 potassium nitrite in deionized water. Add 2.0ml chloroform and dilute to 1.0 liter. Stable for 6 months if refrigerated.

6.3. Standards Preparation:

6.3.1. Prepare Nitrite standard using nitrite stock solution in 100 ml of water.

| Standard Sol'n (ul) | Concentration (ppm) |
| --- | --- |
| 0 | 0 |
| 10 | 0.10 |
| 20 | 0.20 |
| 50 | 0.50 |
| 80 | 0.80 |
| 100 | 1.00 |

6.3.2. Prepare Nitrate standards using nitrate stock solution in 100ml water.

| Standard Sol'n (ul) | Concentration (ppm) |
| --- | --- |
| 0 | 0 |
| 10 | 0.10 |
| 20 | 0.20 |
| 50 | 0.50 |
| 80 | 0.80 |
| 100 | 1.00 |

7. PRESERVATION AND HANDLING

7.1. Nitrite determinations must be performed on an unpreserved sample refrigerated to 4°C. The holding time is 48 hours.

1.1. Nitrate determinations ~~can~~ must be performed ~~two ways:~~ on an unpreserved sample refrigerated to 4°C. The holding time is 48 hours.

7.2. Nitrate plus Nitrite can be performed on a sample preserved to pH<2 with Sulfuric Acid and refrigerated to 4°C. The holding time is 28 days.

8. SAFETY

8.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS__

None

8.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure | Signs and symptoms of exposure |
| --- | --- | --- | --- |

| | | Limit (2) | |
|---|---|---|---|
| Ammonium Hydroxide | Corrosive Poison | 50 ppm-TWA | Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes. |
| Chloroform | Carcinogen Irritant | 50 ppm Ceiling | Acts as a relatively potent anesthetic. Irritates respiratory tract and causes central nervous system effects, including headache, drowsiness, dizziness. Causes skin irritation resulting in redness and pain. Removes natural oils. May be absorbed through skin. Vapors cause pain and irritation to eyes. Splashes may cause severe irritation and possible eye damage. |
| Phosphoric Acid | Corrosive | 1 Mg/M3 TWA | Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage. |
| Potassium Nitrate | Oxidizer | None | Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 9. PROCEDURE

### 9.1. Nitrate Analysis:

9.1.1. Filter well-mixed sample through glass fiber filter and use $NH_4OH$ or HCl to adjust pH = 5 - 9.

9.1.2. Label another two sets of specimen cups, one for nitrite (if not previously analyzed) and another for the sample/buffer solution. Note: Nitrite can be analyzed separately.

9.1.3. Use 100 ml graduated cylinders for each sample. Fill graduated cylinder to 75 ml with buffer solution and add sample to bring to 100 ml.

9.1.4. Pour contents of graduate cylinder into specimen cup to mix.

9.1.5. If nitrite background has not been previously measured, pour 25 ml of sample/ buffer mix into nitrite cup and add 2.0 ml of color indicator to background without passing

through column. ( works well to colorize all background samples at same time)

9.1.6. Pour first 25 ml of sample/buffer through column and allow to drain into waste beaker. Pour remaining 50 ml through column and allow to drain at a fast drip into a pre-rinsed 50ml graduate. (When eluting standards start with highest standard first and work down to zero standard last.)

9.1.7. Pipet 4.0 ml of color indicator into empty specimen cup previously holding sample/ buffer solution.

9.1.8. Turn off stopcock valve when 50 ml has drained into the 50 ml graduate and transfer a portion into the specimen cup with color indicator.

9.1.9. If color darkens rapidly beyond the 1.0 ppm standard, recolorize a smaller portion diluted to 50 ml with water, if not pour the remaining contents of the graduate into the cup.

9.1.10. Write time on cup that sample finished dripping through column.

9.1.11. Color reagent must be added 10 min or less after going through column. Keep Cd in column under fluid in order to avoid air entrapment, which restricts flow, and causes oxidation of Cu coated Cd.

9.1.12. Rinse 50-ml graduate cylinder well with deionized water.

9.1.13. Continue eluting samples through reduction column while monitoring time on cups to analyze after about 20 minutes of colorization. Note: Keep reading times consistent.

9.1.14. Read absorbance of sample in spectrometer at 540nm. Read absorbance of nitrite sample also and record in lab book.

9.1.15. Color tends to settle upon standing. Mix or swirl before reading on spectrometer.

9.1.16. One nitrite standard should also be analyzed with each run to check efficiency of elution column. Follow procedure (without elution) for analysis.

9.2. Nitrite Analysis:

9.2.1. This method should be performed if nitrite analysis is requested OR if nitrite backgrounds are being checked prior to analysis of nitrate.

9.2.2. Measure 75 ml of buffer solution and add 25 ml of sample or standard into cup. Mix well.

9.2.3. Measure 50ml of the previous mixture into a cup.

9.2.4. Add 4 ml of color indicator and wait 10 - 30 minutes for color development. Note: Keep colorizing times consistent.

9.2.5. Read absorbances at 540 nm and record in logbook. Calibrate instrument with blank and 5 standards.

9.2.6. Analyze a background without color indicator for samples when nitrite values must be reported.

9.3. Data Processing:

9.3.1. Calculations:

9.3.1.1. Enter absorbances and dilution recorded in workbook into computer spreadsheet.

9.3.1.2. Run linear regression making sure correlation coefficient is greater than 0.997.

9.3.1.3. Record results in workbook and onto analyte sheets from computer spreadsheet.

9.3.2. *Reporting:*

9.3.2.1. Place analyte sheets into job folders and sign chronicles.

9.3.2.2. Fill out and submit to laboratory manager quality control sheets as required.

9.3.2.3. Notify wet chemistry supervisor if quality control limits are exceeded.

10. QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed.

10.1.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water and process through the entire analytical method. MDLs should be determined yearly.

10.2. Samples are separated into QA batches. This does not include the blank, matrix spike or matrix spike duplicate samples and Laboratory Control Sample. Open a quality control batch every two weeks or every 20 samples, whichever is first.

10.3. For each QA Batch the following procedures must be performed:

10.3.1. A blank must be analyzed each time samples are analyzed. Use deionized water for the blank. The results must be below the reporting limit.

10.3.2. A Laboratory Control Sample is obtained from an outside vendor and is used to measure method performance on the matrix being analyzed.

10.3.3. Two portions of the same sample (matrix spike and matrix spike duplicate) are spiked with nitrate/nitrite. The recovery and relative percent difference must be within laboratory generated control limits. Calculate Recoveries

and RPD as follows:

$$\% \text{ Recovery} = \frac{\text{MS(or MSD) result} - \text{sample conc}}{\text{Amount spiked}} \times 100$$

$$\text{RPD} = \frac{2 \times (\text{ppm MS} - \text{ppm MSD}) \times 100}{(\text{ppm MS} + \text{ppm MSD})}$$

10.4. Instrument calibration should be verified in the following manner:

10.4.1. The standard curve correlation coefficient must be greater than or equal to 0.997.

10.4.2. After initial calibration, every 10 samples and after last sample, a midpoint standard and blank will be analyzed. Verify ICV/CCV are 90-110% of value and ICB/CCB are below the reporting limit.

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLILNG OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated(flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of

the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage.

13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

14. DEFINITIONS

14.1. Refer to document DEFDOC-04 for definitions.

15. REFERENCES

15.1. Standard Methods for the Examination of Water and Wastewater, 18th Edition, American Public Health Association, Baltimore Maryland, 1992, SM 4500 $NO_3$ E.

15.2. Methods for Chemical Analysis of Water and Wastewaters, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; Test Method 353.3.

| STL Edison Standard Operating Procedure | Revision Date: April 1, 2004 |
|---|---|
| Title: CHLORIDE, Analysis of Chloride in Water and Wastewater and Soil<br>Laboratory Director: _____<br>Technical Director: _____<br>QA Manager: _____<br>Department Manager: _____<br>File Location: f:\qaqc\sops\nelac\nelac sops 2004\140wetch\general\cltit04.doc | SOP Number Cltit04<br>Revision 2<br>Page 1 of 7 |

1. SCOPE AND APPLICATION

1.1. Methods SM 4500 CL B and SW846 9253 are applicable to waters and modified for the analysis of soils for chlorides.



2. METHOD SUMMARY

2.1. This method uses silver nitrate as a titrant to quantitatively precipitate chloride out of solution as silver chloride. In the presence of potassium chromate as indicator a red precipitate of silver chromate forms. Each time samples are ran a method blank Laboratory control sample and a blank spike are analyzed and the result must be less than the reporting limit. Each batch of 20 samples or less a laboratory control sample, blank spike, matrix spike, matrix spike duplicate are performed. The results are compared to laboratory generated limits.

3. INTERFERENCES

3.1. Bromide, iodide, and cyanide appear as false amounts of chloride.

3.2. Ortho-phosphate over 25mg/l gives false positive values.

3.3. Iron over 10mg/l interferes by masking the endpoint.

3.4. The analyst must recognize and be consistent with endpoint detection. Endpoint detection is difficult with colored, turbid, or dirty samples. Filter and dilute if necessary.

3.5. Do not use $Al(OH)_3$ as advised in Method 4500 CL B because the blank is too high.

3.6. Sulfide, sulfite, or thiosulfate interfere but can be removed by oxidizing with hydrogen peroxide to sulfate. Test samples with lead acetate paper.

4. APPARATUS AND MATERIALS

4.1. 25ml Buret, Class A

4.2. Magnetic Stirrer and magnetic stir bars

4.3. 200ml evaporating dish

5. REAGENTS

5.1. Sodium hydroxide, 1.25N: Dissolve 50g NaOH in deionized water and dilute to 1000ml.

5.2. Sulfuric Acid, 1N: Dilute 28ml conc. $H_2SO_4$ to 1000ml with deionized water.

5.3. Hydrogen peroxide, 30%.Purchased commercially.

5.4. Indicator Solution: Dissolve 50.0g potassium chromate in distilled water. Add standard silver nitrate titrant until a red precipitate forms. Let stand overnight. Filter and dilute to 1000ml with deionized water.

6. STANDARDS

6.1. Standard Chloride (500mg/l): Dissolve 0.824g NaCl (dried at 140°C) in deionized water and dilute to 1000ml.

6.2. Standard Silver Nitrate Titrant: Dissolve 2.395g silver nitrate in deionized water and dilute to 1000ml (0.0141N). Standardize with NaCl.

7. PRESERVATION AND HANDLING

7.1. Preserve by refrigerating at 4°C.

7.2. The holding time for chloride is 28 days.

8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SAFETY CONCERNS OR REQUIREMENTS

None

8.5 PRIMARY MATERIALS USED

There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

9. PROCEDURE

9.1. Place 100ml of sample in a large evaporating dish and use a magnetic stirrer for stirring. Use lead acetate paper to determine whether hydrogen peroxide should be used to eliminate sulfide, sulfite, or thiosulfate. If present, add 1.0ml of 30% hydrogen peroxide. NOTE: For soils, use 100ml of ASTM leachate prepared as per the LDIASTM1 SOP.

9.2. If sample has color or particulate matter, filter through a 0.45um.

9.3. Check sample with pH paper or pH meter to verify pH = 7-10. If out of range, add NaOH or $H_2SO_4$ accordingly.

9.4. Add 5.0ml indicator solution for every 100ml of sample.

9.5. Titrate with standard silver nitrate until yellow potassium chromate changed to red silver chromate. Samples with considerable amounts of chloride will develop a white precipitate of silver chloride causing turbidity before endpoint. Note: Be consistent with endpoint identification. If uncertain of endpoint prepare several aliquots of standard to practice identifying endpoint.

9.6. FOR SAMPLES REQUIRING *SW846 (9253)* METHOD, REPEAT THE PROCEDURE DESCRIBED IN SECTION 9 USING ONE HALF OF THE ORIGINAL SAMPLE DILUTED TO 100 ml WITH DEIONIZED WATER.

9.7. Data Processing:

9.7.1. Calculations for Chloride in Water Samples:

9.7.1.1. Chloride (mg/l) = $\frac{(A - B) \times N \times (35450)}{C}$

A = titrant vol. (ml) for sample
B = titrant vol. (ml) for blank
C = sample vol. (ml)
N = normality of titrant

9.7.2. Calculations for Chloride in Soil Samples

9.7.2.1. Chloride (mg/Kg) =
$\frac{(A - B) \times N \times (35450)}{C} \times 20 \times$ (100/% Solid)

A = titrant vol. (ml) for sample
B = titrant vol. (ml) for blank
C = sample vol. (ml)
N = normality of titrant

9.7.3. Reporting:

9.7.3.1. Record results in workbook.

9.7.3.2. Place analyte sheets in job folders and sign chronicles.

9.7.3.3. Notify supervisor if quality control limits are exceeded.

9.7.3.4. Submit quality control sheets to manager as required for each batch.

10. QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed.

10.1.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water and process through the entire analytical method. MDLs should be determined yearly.

10.2. Samples are separated into QA batches. This does not include the blank, matrix spike, matrix spike duplicate, and Laboratory Control

Sample. Open a quality control batch every two weeks or every 20 samples, whichever is first.

10.3. For each QA Batch the following procedures must be performed:

10.3.1. A blank must be analyzed each time samples are analyzed. Use deionized water for the blank. The results must be below the reporting limit.

10.3.2. A Laboratory Control Sample is obtained from an outside vendor and is used to measure method performance on the matrix being analyzed. LCS is run daily for maximum of up to 20 samples.

10.3.3. A duplicate is analyzed by using a second aliquot of sample. The relative percent difference (RPD) must be within laboratory generated control limits. Calculate the RPD as follows:

$$RPD = \frac{(\text{ppm Sample} - \text{ppm Duplicate})}{(\text{ppm Sample} + \text{ppm Duplicate})/2} \times 100$$

10.3.4. Two portions of the same sample (matrix spike and matrix spike duplicate) are spiked with 25 ppm of chloride. The recovery and relative percent difference must be within laboratory generated control limits. MS/MSD recoveries must be within 92.7-108%. Relative % difference is set at 5.0. Calculate Recoveries and RPD as follows:

$$\% \text{ Recovery} = \frac{(\text{MS or MSD result} - \text{sample conc.})}{\text{Amount spiked}} \times 100$$

$$RPD = \frac{(\text{ppm MS} - \text{ppm MSD})}{(\text{ppm MS} + \text{ppm MSD})/2} \times 100$$

10.3.5. A spike blank must also be run for each QA batch. Spike this with the same amount as the MS and MSD and use deionized water for the spike blank. The recovery must be within laboratory generated control limit.

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

preparation volumes should reflect anticipated usage and reagent stability.

13. METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2. All MDL results are available on file.

14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

15. REFERENCES

15.1. Standard Methods for the Examination of Water and Wastewater , 18th Edition, American Public Health Association, Baltimore Maryland, 1992, SM 4500 CL B.

15.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed., U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1995; SW846 Method 9253.

1. SCOPE AND APPLICATION

1.1. Methods EPA 375.4 and SW846 9038 are described in this SOP for the analysis of sulfate. This SOP is applicable for the analysis of waters and soils.

2. METHOD SUMMARY

2.1. Sulfate ions form a precipitate in a strongly acidic medium with barium chloride. The turbidity formed by this suspension is measured photometrically at 405 nm and compared with appropriate solutions. Each time samples are analyzed a method blank and laboratory control sample (LCS) are analyzed. The method blank must be less than the reporting limit. The LCS must be recovered within the laboratory generated control limits. A matrix spike and matrix spike duplicate are analyzed with each batch. The recovery and RPD must be within laboratory generated control limits. An ICV and CCV are analyzed at the beginning, end and every four samples and there must be a recovery of ± 10% of the true value. An ICB and CCB are analyzed at the beginning, end and every four samples. The results must be less than the reporting limit.

3. INTERFERENCES

3.1. Silica in concentrations above 500mg/l will interfere with this method.

3.2. Color and turbidity must be accounted for with sample background analysis.

3.3. Sample may be filtered if oily or dirty.

4. APPARATUS AND MATERIALS

4.1. Discreet Analyzer

4.2. Reagent Vessels, 20 ml and 60 ml capacity

4.3. Sample cups (2.0 ml)

4.4. Acrylic multi-cell cuvettes

4.5. Class A volumetric flasks

4.6. Automatic pipettes

4.7. Transfer pipettes

4.8. Filter Apparatus with 0.45 µm filter paper

5. REAGENTS

5.1. Barium chloride, crystals: 20-30 mesh. [$BaCl_2$]

5.2. Sodium Chloride [NaCl]

5.3. Conc. Hydrochloric Acid [HCl]

5.4. Gelatin

5.5. Precipitating Solution: Dissolve 10.0 g Barium Chloride, 20 g Sodium Chloride and 0.5 g Gelatin in 300 ml distilled water (Gently boil the water before adding the gelatin. This will help the gelatin to completely dissolve). **Carefully** add 5 ml of conc. Hydrochloric Acid and dilute to 1000 ml with distilled water. Solution is stable for six months.

6. STANDARDS

6.1. Stock Sulfate Standard (1000 mg/l $SO_4$): Pre-dry sodium sulfate at 250°C for 2 hours. Dissolve 1.479g anhydrous $Na_2SO_4$ in deionized water and dilute to 1000ml. Stable six months.

6.2. Secondary Stock Standard (1000 mg/l $SO_4$): Prepare the same as above but use a different source.

7. SAMPLE HANDLING AND PRESERVATION

7.1. Samples must be maintained at 4°C until the time of analysis.

7.2. The holding time for sulfate is 28 days from the time of sample collection.

7.3. Soils are analyzed by ASTM leachate extraction prior to analysis.

7.4. For sample homogenization refer to SOP Subspl04.

8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

8.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Hydrochloric Acid | Corrosive Poison | 5 ppm-Ceiling | Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. |
| Barium Chloride | Poison Irritant | 0.5 mg/m3 TWA | May be fatal if swallowed. Harmful if inhaled. Avoid contact with eyes, skin, and clothing. Avoid breathing dust. Keep container closed and when in use adequate ventilation. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 9. PROCEDURE

9.1. Refer to the Discreet Analyzer Instrument Manual to perform all daily maintenance checks to ensure proper validity of machine including a manual QC run to ensure a valid calibration. In the reagent menu, click on the reagents used in the parameter and check the available levels and expiration dates. Change or add if necessary.

9.2. Once a day prior to analysis, perform the "Start up" function and "Water blank check."

9.2.1. Start up function.

9.2.1.1. From the main menu, click on *"Start up needed"* (located at the uppermost left corner of the screen). Click *"ok"* to the pop up question. In this procedure, the injecting needle and all tubes will be rinsed and washed. ANALYSIS WILL NOT START IF "START UP" HAS NOT BEEN PERFORMED.

9.2.2. Run Water blank check after "Start up" is performed.

9.2.2.1. From the main menu, click on the following buttons in this order: F8 (more), F2 (Instr. action), F1 (Perform Water Blk). The instrument will now measure the absorbance of each cuvette for every wavelength and calculates the standard deviation (SD) for each of those wavelengths in mA. This will take approximately 2-3 minutes.

9.2.2.2. Check that the resulting SD (mA) of each wavelength is below 2 mA. If SD is greater than 2 mA, repeat Water blank check (9.2.2.1.) or refer to the instrument manual for proper cleaning maintenance (i.e. clean/wash needle, change DI water supply). If SD (mA) is below 2 mA, then run the calibration standards or the initial calibration checks (ICV/ICB), whichever applies.

9.3. Prepare calibration standards by adding the amount specified below to 100ml volumetric flasks and bringing to volume with deionized water. **Calibration is valid for one month.**

| Discreet Analyzer Name | Standard (ml) | Concentration $SO_4$ (mg/l) |
| --- | --- | --- |
| SO4-0 | 0.0 | 0 |
| SO4-1 | 0.5 | 5 |
| SO4-2 | 1.0 | 10 |
| SO4-3 | 1.5 | 15 |
| SO4-4 | 2.0 | 20 |
| SO4-5 | 2.5 | 25 |
| SO4-6 | 3.0 | 30 |
| SO4-7 | 4.0 | 40 |

9.4. Load standards, ICV-SO4, and ICB into the segment. In the Sample Entry screen click F8, then the "Sample Segment" button. Begin entering the standards into the correlating positions (use the pull down menu to enter the standard and control names). Once

everything has been entered, insert the segment and return to the main menu. Click the "Calibration/QC Selection" button and highlight "Sulfate-Test." Check the status of all the necessary controls; this is designated by "OK" or "Missing." If the status is "OK" click on the "Calibration" button. The status of your calibration will now change to "pending." Return to the Main screen and push the start button on the keyboard. **Note:** you can only start an analysis when you are in the Main Screen.

9.5. After the calibration has completed, you can either accept or reject and rerun the calibration. If accepted, continue with the samples.

9.6. Enter all samples, including any QA's, CCV, and CCB to be run in the Sample Entry screen. Print out a sample segment preparation sheet by first clicking F8, then F1 "Print Screen." Repeat this process for each segment. **Include manual dilutions of 20x for soil samples**

9.7. Shake samples and pour in labeled cups and allow for the sample to settle out any particulates. For soils, use ASTM leachate prepared as per the LDIASTM1 SOP.

9.8. If sample still has color or particulate matter, filter through a 0.45µm or centrifuge.

9.9. Using transfer pipettes, transfer the supernatant of the sample or the filtered sample to the sample cups in the position indicated by the sample segment preparation sheet.

9.10. Load the segments into the Discreet Analyzer and assign the test parameter (Sulfate Test and Sulfate 405 ie. kinetics). Return to the main page and press start. Continue loading the segments and inserting them into the machine, once the machine has been started it is not necessary to hit the start button if more segments are loaded while analyzing.

9.11. A CCV and CCB are **run after every four samples** and at the beginning and end of a run. These controls must be entered as samples, assign numbers to each set.

9.12. Results:

9.12.1. Check the results, make any necessary dilutions either manually or have the analyzer do this. Be sure to check the kinetics for each sample, (kinetics do not need to be run on control samples). If the kinetics fail, reran the sample, either straight or with a dilution, or filter if necessary. Double check all controls.

9.12.2. Print out results and click the "Accept" button.

9.13. Data Processing

9.13.1. Calculations for Soil Samples:

9.13.1.1. Sulfate(mg/kg)=
Result from Discreet Analyzer X (100/% Solid)

9.13.1.2. Print report from Discreet Analyzer

9.13.1.3. Update Data in the LIMS system

9.13.1.4. Submit data packages to manager as required for each batch.

9.13.2. Results:

9.13.3. Submit data packages to manager as required for each batch.

9.13.3.1. Notify supervisor if quality control limits are exceeded.

9.13.3.2. Submit analyte sheets and notify Wet Chemistry supervisor if quality control limits are exceeded.

9.13.3.3. Transfer results to analyte sheets. Place analyte sheets with spreadsheets in job folders and sign chronicles.

9.13.3.4. Notify supervisor if check standards or quality control samples exceed limits.

9.13.3.5. Submit quality control sheets to manager as required for each batch.

10. QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed.

10.1.1. Method Detection Limit (MDL) – The MDL must be determined prior to the analysis of any sample. This MDL is established by analyzing seven replicate aliquots of the fortified reagent spiked with three to five times the established detection limit. These aliquots are carried through the entire analytical procedure. MDLs are determined annually.

10.2. Water/Soil samples are separated into separate QA batches. This does not include the method blank, matrix spike, matrix spike duplicate and LCS. Open a quality control batch every two weeks or every 20 samples, whichever is more frequent.

10.3. For each QA Batch the following procedures must be performed:

10.3.1. A method blank must be analyzed each time samples are analyzed. One method blank is assigned for every 20 samples and the results must be below the reporting limit. Use deionized water for the blank.

10.3.2. A Laboratory Control Sample is obtained from an outside vendor and is used to measure method performance on the matrix being analyzed. LCS is run daily or every 20 samples whichever is more frequent. It must be within the vendor's specified limits.

10.3.3. Two portions of the same sample (matrix spike and matrix spike duplicate) are spiked with 20 ppm of the primary Sulfate standard. The recovery and relative percent difference must be within laboratory generated control limits. Calculate Recoveries and RPD as

follows:

$$\%Recovery=\frac{(MS\ or\ MSD\ result\ -sample\ conc.)}{Amount\ spiked} \times 100$$

$$RPD=\frac{(ppm\ MS\ -\ ppm\ MSD)}{(ppm\ MS + ppm\ MSD)/2} \times 100$$

10.4. Instrument calibration is verified in the following manner:

10.4.1. The calibration curve must be verified by analyzing an Initial Calibration Verification (ICV) solution prepared at 20 ppm. The solution is derived from the secondary sulfate standard. The value obtained must be within ± 10% of the true value. If the value measured is outside of the acceptance limits, the problem must be corrected, the instrument recalibrated and the ICV reanalyzed and be within the acceptance limits.

10.4.2. The validity of the calibration curve is checked periodically by a Continuing Calibration Verification (CCV); this solution is analyzed every 4 samples and after the final sample. "Samples" include method blank, matrix spike, matrix spike duplicate, LCS, and environmental samples. The measured value cannot differ by ± 10% of the true value. The true value is the same as the ICV (20 ppm) and is derived from the same source. If CCV fails, the previous 4 samples following the last passing calibration must be reanalyzed and be within the acceptance limits.

10.4.3. Following each calibration verification, a calibration blank must be analyzed. This includes an ICB (Initial Calibration Blank) and CCB (Continuing Calibration Blank); the results must be less than the reporting limit or previous 4 samples must be reanalyzed.

## 11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see "*Out of Control Events Corrective Actions*" SOP.

## 12. WASTE MANAGEMENT AND POLLUTION PREVENTION

### 12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

### 12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

13. METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

15. REFERENCES

15.1 Methods for Chemical Analysis of Water and Wastewaters, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; Test Method 375.4

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed., U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1995; SW846 Method 9038.

| STL Edison Standard Operating Procedure | Revision Date: April 1, 2004 |
|---|---|
| Title: ALKALINITY, Analysis of Alkalinity in Water and Wastewater<br>Laboratory Director: _____<br>Technical Director: _____<br>QA Manager: _____<br>Department Manager: _____<br>File Location: f:\qaqc\sops\nelac\nelac sops 2004\140wetch\general\alktw04.doc | SOP Number Alktw04<br>Revision 2<br>Page 1 of 7 |

UNCONTROLLED COPY

1. SCOPE AND APPLICATION

1.1. Methods 310.1 and SM 2320B are applicable to drinking, surface waters, saline waters, domestic and industrial wastes.

1.2. The sample aliquot should be selected such that the titration volume used do not exceed 50ml.

2. METHOD SUMMARY

2.1. The quantity of alkalinity contained in a sample is determined by titrating with acid to a pH of 8.3 (if applicable) and then to 4.5. For each batch of 20 samples or less, a method blank, laboratory control sample, and duplicate must be performed. The results must be within the laboratory control limits.

3. INTERFERENCES

3.1. Dissolved gas can affect alkalinity, prevent undo agitation or exposure to atmosphere as much as possible.

4. APPARATUS AND MATERIALS

4.1. pH meter

4.2. Burette, 10 ml and 25 ml. (Class A)

4.3. Erlenmeyer flasks, 250 ml and 500 ml

4.4. Magnetic stirrer and Teflon-coated magnets

4.5. Volumetric pipets, assorted (Class A)

4.6. Volumetric flasks, assorted (Class A)

4.7. Hotplate

5. REAGENTS

5.1. 0.05 N. Sodium carbonate solution: Place 0.625 grams $Na_2CO_3$ (dried 4 hours at 250°C) in a 250 ml volumetric flask and dilute to mark with deionized water. Solution is good for one week.

5.1.1. 0.10 N. Sulfuric Acid: Purchased commercially. Standardized against $Na_2CO_3$ solution.

5.2. 0.02 N. Sulfuric Acid: Purchased commercially. Standardized against $Na_2CO_3$ solution.

6. STANDARDS

6.1. Standardize titrants every two weeks by the following:

6.1.1. 0.1 N. $H_2SO_4$-

6.1.1.1. Place 40.0 ml freshly prepared 0.05 N. $Na_2CO_3$ solution into a 500 ml erlenmeyer flask. Add about 60 ml of deionized water.

6.1.1.2. Titrate with 0.1 N. $H_2SO_4$ until pH = 5.0.

6.1.1.3. Cover flask with a watchglass and boil for 3 minutes.

6.1.1.4. Cool and continue titrating to pH 4.5.

6.1.2. 0.02 N. $H_2SO_4$

6.1.2.1. Same as above except use only 15.0 ml $Na_2CO_3$ solution and bring up to 100 ml with deionized water.

6.1.3. Titrant Concentration (N.) = $\frac{2.50 \times A}{53.00 \times B}$

A = vol. $Na_2CO_3$ solution (ml)
B = vol. titrant (ml)

7. PRESERVATION AND HANDLING

7.1. Do not dilute, filter, concentrate, or alter samples in any way.

7.2. Preserve by refrigerating at 4°C and limit headspace. Holding time is 14 days but strongly urged to analyze as soon as possible.

8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

There are no specialized safety concerns associated with this method.

8.5. PRIMARY MATERIALS USED

There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

9. PROCEDURE

9.2. Rinse all glassware well with deionized water.

9.3. Transfer 100 ml or aliquot of a well-mixed sample to specimen cup with as little agitation as possible.

9.4. Record initial pH of sample.

9.5. Titrate to 8.3 if carbonate and bicarbonate alkalinity is required, and proceed to next step.

9.6. Titrate with standardized acid to pH of 4.5 and record volume of acid. Sample may be swirled to mix in acid, but avoid excessive agitation. If alkalinity is $<20$ppm use 0.02N $H_2SO_4$.

**9.7. If alkalinity is less than 20 ppm, continue to titrate to 4.20 and note added titrant.**

9.8. Procedure for All forms of Alkalinity

9.8.1. Follow Procedures for Total Alkalinity. If pH of initial sample is greater than 8.3, titrate initially to a pH of 8.3 and record volume of titrant in logbook. This will be equal to P (or the phenolphthalein alkalinity) in the calculations. Then continue titrating to a pH of 4.5 and record in logbook.

9.9. Calculations:

9.9.1. Total Alkalinity:

9.9.1.1. $$\text{Alkalinity (mg/l } CaCO_3) = \frac{A \times N \times 50000}{B}$$

A = volume of acid, ml.
N = concentration of acid, N.
B = volume of sample, ml.

9.9.2. Total Alkalinity low level, < 20 mg/l)

9.9.2.1. $$\text{Alkalinity} = \frac{(2A - B) \times N \times 50000}{C}$$

A = vol. acid to pH = 4.5, ml.
B = vol. acid from pH = 4.5 to 4.2, ml.
C = vol. of sample, ml.

9.9.3. Calculations for All Forms of Alkalinity:

9.9.3.1. Carbonate alkalinity is present when phenolphthalein alkalinity is not zero but less than total. Hydroxide alkalinity is present if phenolphthalein alkalinity is more than half the total. Bicarbonate alkalinity is present if phenolphthalein alkalinity is zero or less than half the total.

9.9.3.2. Calculate different forms of alkalinity using relationships in chart below:

| Result of Titration | Hydroxide as CaCO3 | Carbonate as CaCO3 | Bicarbonate as CaCO3 |
| --- | --- | --- | --- |

| | | | |
| --- | --- | --- | --- |
| P = 0 | 0 | 0 | T |
| P < 0.5T | 0 | 2P | T - 2P |
| P = 0.5T | 0 | 2P | 0 |
| P > 0.5T | 2P - T | 2(T - P) | 0 |
| P = T | T | 0 | 0 |

Where P = phenolphthalein alk. and T = total alk.

9.10. Reporting:

9.10.1.1. Record results in workbook.

9.10.1.2. Place analyte sheets in job folders and sign chronicles.

9.10.1.3. Notify supervisor if quality control limits are exceeded.

9.10.1.4. Submit quality control sheets as required for each batch.

10. QUALITY CONTROL

10.2. Prior to the analysis of any samples the following must be performed.

10.2.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water and process through the entire analytical method. MDLs should be determined yearly.

10.3. Samples are separated into QA batches. This does not include the blank, duplicate sample and Laboratory Control Sample. Open a quality control batch every two weeks or every 20 samples, whichever is first.

10.4. For each QA Batch the following procedures must be performed:

10.4.1. A blank must be analyzed each time samples are analyzed. Use deionized water for the blank and the results must be below the reporting limit.

10.4.2. A Laboratory Control Sample is obtained from an outside vendor and is used to measure method performance on the matrix being analyzed. LCS is run daily.

10.4.3. A duplicate is analyzed by using a second aliquot of sample. The relative percent difference (RPD) must be within laboratory generated control limits. Calculate the RPD as follows:

$$RPD = \frac{2(\text{ppm Sample} - \text{ppm Duplicate})}{(\text{ppm Sample} + \text{ppm Duplicate})} \times 100$$

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

12.3. Waste Streams Produced by the Method

There are no special waste streams associated with this method.

13. METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

15. REFERENCES

15.1 Methods for Chemical Analysis of Water and Wastes, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; Test Method 305.1.

15.2 Standard Methods for the Examination of Water and Wastewater , 18th Edition, American Public Health Association, Baltimore Maryland, 1992, SM 5530 B+D.

| STL Edison Standard Operating Procedure | Revision Date: 04/28/04 |
|---|---|
| Title: Methane, Ethene, Ethane and Propane by GC FID Using Static Headspace, Method 3810 (modified), SW846, Rev. 0, Sept. 1986 | Revision 5 |
| Laboratory Director: _____ | SOP Number 3810M04 |
| Technical Director: _____ | Page 1 of 11 |
| QA Manager: _____ | |
| Department Manager: _____ | |
| File Location: F:\QAQC\SOPS\NELAC\NELAC SOPs 2004\105voagc\SW846\3810M04.DOC | |

UNCONTROLLED COPY

## 1. SCOPE AND APPLICATION

1.1. Method 3810 is a static headspace technique of sample introduction followed by GC-FID analysis of volatile organic compounds.

1.2. In this application, Method 3810 is used to analyze aqueous samples for Methane, Ethene, Ethane and Propane.

1.3. The estimated quantitation limits for this method is approximately 5 ug/l.

## 2. METHOD SUMMARY

2.1. An aliquot of sample is introduced to the platen-heated zone and allowed to equilibrate. The sample is mixed and heated for a period of time, allowing the volatile components to equilibrate in the headspace above the sample. The sample vial is raised onto the needle, puncturing the septum. Pressurization gas fills the vial. Once pressurization has stopped, the vent is opened, and the sample vapor exits through the sample loop. The loop is backflushed with carrier gas, sweeping the sample through the heated transfer line onto the GC column, where the analytes are chromatographically separated and detected with a flame ionization detector.

2.2. Concentrations are calculated for each component in a sample by comparing the area of response to the area found in a standard of known concentration.

## 3. INTERFERENCES

3.1. This method is susceptible to contamination from a number of sources. Potential sources of contamination include organic solvents used in other laboratory procedures, improper cleaning of sample handling equipment, and carryover from high level samples. Steps have been taken to ensure that these potential problems are eliminated from the laboratory.

3.2. The volatile laboratory has been moved to a separate building, away from the organic extraction area where large quantities of organic solvents are used. No organic solvents are used or stored in the volatile laboratory.

3.3. Proper sample handling techniques are utilized to minimize contamination problems.

3.4. Carryover can occur anytime a high level sample is analyzed. The sample analyzed after a high level sample is inspected carefully for signs of carryover, and re-analyzed if necessary. If this sample does not contain any of the compounds found in the high level sample, the system can be considered contamination free.

4. APPARATUS AND MATERIALS

4.1. Vials. 20-ml autosampler vials, Microliter Analytical Supplies, p/n 20-2000.

4.2. Caps with butyl rubber septa. For 20-ml autosampler vials, Microliter Analytical Supplies, p/n 20-0030A.

4.3. Crimping tool.

4.4. Microsyringes. 10 ul to 1000 ul.

4.5. Syringes. 5 and 10 ml gas tight.

4.6. Eppendorf pipette. 20 ul and 200 ul size.

4.7. Vials. 2-ml and 10-ml amber glass with screw cap and Teflon-faced septa.

4.8. Headspace analyzer. Tekmar 7000 with 7050 carrousel autosampler.

4.9. Gas Chromatograph. HP 5890 GC, with temperature programming capability, equipped with flame ionization detector (FID).

4.10. GC column. 30 m x 0.53 mm ID, J&W GS-Q capillary column.

4.11. Data system. HP Chemstation II for data acquisition, Target software for data processing.

5. REAGENTS

5.1. Reagent water. Distilled water purchased from Poland Spring.

6. STANDARDS

6.1. A stock standard gas mix is purchased from Scott Specialty Gases. Each component (Methane, Ethene, Ethane and Propane) is at a concentration of 1% in nitrogen.

7. PRESERVATION AND HANDLING

7.1. Samples are collected without headspace in 40-ml VOA vials and preserved to a pH < 2.

7.2. Samples are protected from light and stored at 4° C from time of receipt to time of analysis.

7.3. All samples must be analyzed within 14 days after sample collection.

7.4. If a sample is unpreserved (pH > 2), analysis must be completed within 7 days.

8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2 The analyst should wear the appropriate personal protective equipment including lab coat, safety eyewear, and gloves.

8.3 Any questions pertaining to safety issues or procedures should be brought to the department manager or Edison Safety Officer.

8.4 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

8.5 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for

each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
| --- | --- | --- | --- |
| Methanol | Flammable Poison Irritant | 200 ppm-TWA | A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 9. PROCEDURE

9.1. Instrument operating parameters are set prior to calibration and will remain constant throughout sample analysis.

**Tekmar 7000 Headspace Autosampler**

| | |
| --- | --- |
| Platen Temperature | 65°C |
| Platen Equilibrium Time | 1.0 min |
| Sample Equilibrium Time | 1.0 min. |
| Mix Time | 1.0 min. |
| Mix Power | 3 |
| Pressurization Time | 0.2 min. |
| Pressurization Equilibrium | 0.1 min |
| Stabilization time | 0.1 min |
| Loop Fill Time | 0.4 min. |
| Loop Equilibrium Time | 0.2 min. |
| Injection time | 0.5 min. |
| Transfer Line Backpressure | 15 psi |

**GC/FID Temperature Program**

| | |
| --- | --- |
| Initial temperature | 60°C |
| Run time | 5 min. |

9.2. Initial calibration

9.2.1. The initial calibration is performed by analyzing standards at 5 concentration levels. The calibration concentrations for each analyte are as follows in ug/l:

| Compound | Conc. Level 1 | Conc. Level 2 | Conc. Level 3 | Conc. Level 4 | Conc. Level 5 |
| --- | --- | --- | --- | --- | --- |
| Methane | 3.27 | 16.35 | 32.7 | 65.4 | 130 |
| Ethene | 5.7 | 28.5 | 57.0 | 114 | 228 |
| Ethane | 6.15 | 30.75 | 61.5 | 123 | 246 |
| Propane | 8.95 | 44.75 | 89.5 | 179 | 358 |

9.2.2. Prepare calibration standards in 10mL of reagent water as follows:

| | Level 1 | Level 2 | Level 3 | Level 4 | Level 5 |
| --- | --- | --- | --- | --- | --- |
| Calibration gas | 5 ul | 25 ul | 50 ul | 100 ul | 200 ul |

9.2.3. Add calibration gas to 10ml of reagent water in a crimp-capped 20ml autosampler vial.

9.2.4. Load the vials into the Tekmar 7000 autosampler tray and analyze.

9.2.5. After the standards have been analyzed, transfer the data to the Target network for processing.

9.2.6. Calculate a calibration factor for each compound. A calibration factor is equal to peak area divided by concentration of calibration standard.

9.2.7. Calculate the RSD of the five calibration factors for each target analyte. If the %RSD is ≤20%, the curve is considered linear and the average calibration factor is used for calculating target analytes.

9.3. Calibration verification

9.3.1. The initial calibration must be verified every 12 hours with the analysis of a mid-level calibration standard.

9.3.2. The calibration check sample is prepared by injecting 50 ul of calibration gas into 10 ml of water.

9.3.3. Calculate a calibration factor for each analyte in the check standard. If the %D is ≤15%, the initial calibration is still considered valid and analysis may continue.

9.3.4. If the %D is >15%, repeat the calibration check. If ≤ 15% D cannot be achieved, a new initial calibration must be performed.

9.3.5. Analyze a mid range calibration standard every 10 injections. Evaluate each standard for % D from the initial calibration as per section 9.3.3.

9.4. Blank analysis

9.4.1. Following successful calibration, a blank must be analyzed.

9.4.2. A blank consists of 10mL of reagent water that is analyzed in the same manner as the standards and samples.

9.4.3. The blank must not contain any target analytes at a level greater than the quantitation limit.

9.5. Sample analysis

9.5.1. Inject 10 ml of the aqueous sample into a 20-ml autosampler bottle, cap immediately and analyze.

9.5.2. Transfer data to Target network and process using the calibration factors from the most recent initial calibration.

10. QUALITY CONTROL

10.1. Initial calibration

10.1.1. All target analytes for a particular analysis must be included in the initial calibration standards and calibration verification standards.

10.1.2. The concentrations of the other calibration standards define the working range for this analytical procedure.

10.1.3. Calculate a calibration factor (CF) for each analyte at each concentration level by tabulating peak area responses against concentration.

10.1.4. Calculate the relative standard deviation (RSD) of the CFs for each analyte.

10.1.5. If the RSD is less than 20%, the calibration is considered linear and the average CF can be used for quantitation.

10.1.6. The calculation of sample results will be done using an external standard calibration. The concentration of each analyte in a sample is determined by comparing the peak area to the response for that analyte in the initial calibration.

10.2. Calibration verification

10.2.1. The initial calibration must be verified every 12 hours with the analysis of a mid-range calibration standard.

10.2.2. If the response found in the calibration verification standard is within 15% of the response obtained during the initial calibration, then the initial calibration is still valid.

10.2.3. If the response found in the calibration verification standard exceeds the 15% criteria, the system must be inspected for problems and/or re-calibrated.

10.2.4. Samples calibrated using external standards must be bracketed by standards that meet QC acceptance criteria. A calibration verification standard is analyzed after every 10 injections. This standard must show <15% drift from the initial calibration, or all samples analyzed before this standard must be reanalyzed.

10.3. Blank analysis

10.3.1. Method blanks are analyzed immediately after the calibration standard to ensure that the chromatographic system is clean.

10.3.2. Method blanks must be prepared in the same manner as the associated samples, and also use the same sample introduction technique.

10.3.3. Method blanks must not have any analyte above the quantitation limit.

10.4. Matrix spike/ matrix spike duplicate

10.4.1. Matrix spike/matrix spike duplicate pairs are analyzed at a frequency of one set per 20 samples.

10.4.2. The matrix spike/matrix spike duplicates are prepared from a calibration gas that is a different source than the gas used for the initial calibration.

10.4.3. Prepare a matrix spike by adding 50 ul of calibration gas to a 10-ml sample.

10.4.4. In house spike limits have been established by calculating the percent recovery (p) and the standard deviation(s) for each analyte using 20 representative data points. If there are not enough data points to generate in house limits for a particular matrix or level, the advisory limits of 70% - 130% are used until enough data is collected.

10.4.5. Recovery limits are generated by using (p)±3(s).

10.4.6. New limits are generated annually.

10.4.7. The 2004 limits for MS/MSD are listed below.

| Compound | % Recovery Limits |
| --- | --- |
| Methane | 37 – 155 |
| Ethene | 63 – 148 |
| Ethane | 65 – 148 |
| Propane | 67 – 141 |

10.5. Blank spike analysis

10.5.1. A blank spike is analyzed at a frequency of one per 20 samples.

10.5.2. The blank spike is also prepared from the second source calibration gas.

10.5.3. Prepare the blank spike by adding 50 ul of calibration gas to 10 ml of reagent water.

10.5.4. The blank spike must meet the same recovery limits as the MS/MSD.

10.6 Retention time windows

10.6.1 Establishing retention time windows is crucial for identification of target compounds in any GC method that does not use internal standard calibration.

10.6.2 Retention time windows are used to compensate for minor shifts in retention time due to normal chromatographic variability.

10.6.3 Retention time is monitored in all standards, blanks, samples and QC samples. If retention time for any target or surrogate changes by more than 0.100 minute from the initial calibration or by 0.05 from the calibration verification standard, the system must be inspected for possible malfunctions. If corrective action is required, any samples that were analyzed while the system was out of control must be reanalyzed.

10.6.4 Retention time windows are updated every time a new initial calibration or calibration verification is run.

11. WASTE MANAGEMENT AND POLLUTION PREVENTION

11.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

11.2. POLLUTION PREVENTION:

11.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

11.2.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

12. CALCULATIONS

12.1 Refer to the SOP for Organic Calculations, SOP Number OC03.

13. DEFINITIONS

13.1 Refer to document DEFDOC-04 for definitions.

14. METHOD PERFORMANCE

14.1. A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

14.2 All MDL results are available on file.

15. DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1. Technical acceptance criteria for sample analysis.

15.1.1 The samples must be analyzed on a GC system meeting the initial calibration, continuing calibration and blank technical acceptance criteria.

15.1.2 The sample must be analyzed within the required holding time.

15.1.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

15.1.4 After analyzing a sample that exceeds the initial calibration range the analyst must either analyze an instrument blank (using the same purge inlet if using an auto sampler) which must meet technical acceptance criteria for blank analysis or monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the calibration range.

15.2 Corrective Action for Sample Analysis

15.2.1 Samples must meet technical acceptance criteria before reporting data.

15.2.2 Corrective action for failure to meet initial and continuing calibrations and method blanks must be completed prior to sample analysis.

16. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Reports will be initiated in order to provide for investigation and follow-up.

17. REFERENCES

17.1. Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 0, September 1986, Method 3810, Static Headspace Analysis.

| SOP No. | Revision No. | Date | |
|---|---|---|---|
| AWC-VFA-20 | 1 | February 4, 2004 | Page 1 of 13 |

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

| REVIEWED & APPROVED BY: | Signature | Date |
|---|---|---|
| Christopher Oprandi, Laboratory Director | Christopher Oprandi | 2/5/04 |
| Verl D. Preston, Quality Manager | Verl D Preston | 2/5/04 |
| Peggy Gray-Erdmann, Supervisor | Peggy Gray-Erdmann | 2/10/04 |



## 1.0 IDENTIFICATION OF TEST METHODS

1.1. Volatile Fatty Acids are determined using Dionex proprietary method. This method is a modification to Standards Methods for the Examination of Water and Waste Water 20th ed., Method 5560 Organic and Volatile Acids.

## 2.0 APPLICABLE MATRIX

2.1. This method is applicable to surface water, groundwater, wastewater, drinking waters and soils.

## 3.0 REPORTING LIMIT

3.1. The reporting limit for each acid is listed below:
3.1.1. Acetic Acid – 1 mg/L

3.1.2. Propionic Acid – 1 mg/L

3.1.3. Butyric Acid – 1 mg/L

3.1.4. Lactic Acid – 1 mg/L

3.1.5. Formic Acid – 1 mg/L

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 2 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

3.1.6. Pyruvic Acid – 1 mg/L

3.2. MDLs are calculated every year in accordance with method specification and kept on file with the QA department.

## 4.0 SCOPE AND APPLICATION

4.1. Ion Chromatography provides a single instrumental technique that may be used for the measurement in environmental samples of the common Volatile Fatty acids or Organic acids. Fatty acids are low-molecular weight carboxylic acids. Identification and quantification is performed by Ion chromatography. Separation is accomplished by an ion-exclusion column. Peak sensitivity and lower reporting limits are obtained by using an eluent suppressor. The acids are then identified by conductivity detection.

## 5.0 SUMMARY OF TEST METHOD

5.1. A filtered aqueous sample is injected into an ion chromatograph with the use of an automated sampler. The sample merges with an eluent stream and is pumped through the system. The ion exchanger separates the acids of interest. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

## 6.0 DEFINITIONS

6.1. Standard definitions can be found in section 3.0 of the STL Buffalo Laboratory Quality Manual.

6.2. VFA: Volatile Fatty Acid

## 7.0 INTERFERENCES

7.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the acid of interest. Acids of high concentrations can interfere with the peak resolution of an adjacent acid. Diluting the sample can minimize overlap.

7.2. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 3 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

7.3.1 All samples must be filtered through a 20um filter before injection. If particles contaminate the guard or analytical columns, follow the manufacturer's suggestions for cleaning, or simply replace the column.

**8.0 SAFETY**

8.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

8.2.1. This method uses weak carboxylic acids and heptafluorobutyric acid. All acids will be poured into water.

8.2.2. Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

8.3. PRIMARY MATERIALS USED

8.3.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
|---|---|---|---|
| Heptafluor-Butyric acid | Corrosive | NA | Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain. |
| Fatty Acid Custom Mix 1000ppm in water | Corrosive | NA | May irritate eyes and/or skin. Irritates Respiratory tract. Low blood pressure. Dermatitis. Pulmonary edema. Lung damage. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

**9.0 EQUIPMENT AND SUPPLIES**

9.1. Ion chromatograph complete with all required accessories:

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 4 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

9.1.1. ICE-AS6 separator column capable of resolving weak organic acids.

9.1.2. AMMS-ICE suppressor.

9.1.3. Conductivity detector with temperature control and separate working and reference electrodes.

9.1.4. Pump able to deliver 1.2 ml/min of constant flow rate.

9.1.5. Data collection and analysis system.

9.1.6. Automated sampler.

9.2. Various laboratory glassware such as Class A graduated cylinders, syringes, volumetric flasks and pipettes.

9.3. 10 ml syringes and 0.2 um syringe filters for colored samples

9.4. Analytical balance, capable of weighing to the nearest 0.0001g.

9.5. Filter caps for clean samples purchased from Dionex

9.6. 5 ml sample vials purchased from Dionex

**10.0 REAGENTS AND STANDARDS**

10.1. Sample bottles: Glass or polyethylene bottles of sufficient volume to allow replicate analyses of anions of interest.

10.2. Reagent water: Distilled or deionized water free of the anions of interest. Water should contain particles no larger than 0.20 microns.

10.3. Regenerant Concentrate (TetraButylAmmonium Hydroxide TBAOH) from VWR catalog# (JTV365-7) 0.4M water solution.

10.3.1 Regenerant solution (10mM): Add 50ml of 0.4M TBAOH into 2L reagent water.

10.4. Eluent Concentrate (Heptafluorobutyric acid): 99% Heptafluorobutyric acid is purchased from Aldrich. Catalog # 16,419-4

10.4.1. Eluent Solution (1.0mM.): Weigh 0.21g of the Heptafluorobutyric acid (10.4) to 1 liter with reagent water or 250ul into 2 liter

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 5 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

10.5. Multi analyte Ion Chromatography Custom Standards purchased from Restek & Supelco Scientific. Custom Mix contains 1000mg/l of the following acids: Acetic, Propionic, Butyric, Lactic, Formic, and Pyruvic. The standard source from Supelco is used for the calibration curve (10.6) and the standard source from Restek is used for the ICV/ CCV/LCS Solutions and the matrix spikes (10.7, 10.8, 10.9, 10.10).

10.6. Calibration standards: all are made from dilutions of the Multi Element IC Standards in reagent water.

10.6.1. Prepare the calibration standards for a 5-point curve by measuring the following volumes into a 25 ml Class A volumetric. Bring to the final volume of 25 ml with reagent water.

| | Level 1 | Level 2 | Level 3 | Level 4 | level 5 |
|---|---|---|---|---|---|
| Stock solution (1000 mg/L) | 25ul | 50ul | 125ul | 250ul | 1.25ml |
| | | | | | |
| Final Volume | 25ml | 25ml | 25ml | 25ml | 25ml |

10.6.2 The final concentrations of each anion in the 5 calibration points are summarized below.

| | Level 1 (mg/L) | Level 2 (mg/L) | Level 3 (mg/L) | Level 4 (mg/L) | Level 5 (mg/L) |
|---|---|---|---|---|---|
| Formic | 1 | 2 | 5 | 10 | 50 |
| Propionic | 1 | 2 | 5 | 10 | 50 |
| Butyric | 1 | 2 | 5 | 10 | 50 |
| Lactic | 1 | 2 | 5 | 10 | 50 |
| Formic | 1 | 2 | 5 | 10 | 50 |
| Pyruvic | 1 | 2 | 5 | 10 | 50 |

10.7. ICV/CCV/LCS, MS and SD (MSD) solution: 500ul of the Multi Element IC Standard diluted to 100ml with reagent water. The final concentration for each acid in the solution is as follows:

| | ICV & CCV/LCS |
|---|---|
| Acetic | 5 mg/l |
| Propionic | 5 mg/l |
| Butyric | 5 mg/l |
| Lactic | 5 mg/l |
| Formic | 5 mg/l |
| Pyruvic | 5 mg/l |

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 6 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

## 11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1. Samples should be shipped and stored in 40 mL glass amber vials at 4 ± 2 degrees C. Samples should be analyzed for VFA within 28 days of collection.

11.2. Soil will follow the same preservation and holding times as the water samples, starting from the time of extraction. Soils should be collected in 4 oz. or 8 oz. wide mouth amber jars.

## 12.0 QUALITY CONTROL

12.1. Before analyzing samples, the laboratory must establish a method detection limit (MDL). The MDL is repeated every year.

12.2. Each group of sample analyses must be bracketed by an acceptable calibration verification sample and calibration blank. All quality control data should be maintained and available for easy reference or inspection.

12.3. Initial and Continuing Calibration Blank (ICB, CCB): To determine freedom from contamination, prepare one calibration blank (ICB) at the beginning of the analytical procedure and another (CCB) after every ten samples and at the end of the analytical procedure. The blank consists of 5 ml reagent water that gets the same treatment as the samples and standards. The blanks must be free of the analytes of concern at levels less than the STL Buffalo quantitation limit.

12.3.1. All blanks associated with USACE samples should be less than half the STL Buffalo quantitation limit for each anion.

12.4. Initial and Continuing Calibration Verification/Laboratory Control Sample (ICV/CCV/LCS): Prepare an ICV at the beginning of the analytical procedure and additional CCV/LCS after every ten samples and again at the end of the procedure. The recovery of the ICV/CCV/LCSs must be within 80-120% of the true value.

12.5. Sample Duplicate: Analyze either a Matrix Duplicate (MD) or a Matrix Spike Duplicate (MSD) with every batch of twenty or fewer samples. Acceptable RPD between replicate analyses should be less than 20%.

12.6. Matrix Spikes (MS) are to be run with every batch of 20 or fewer samples. Deviations may occur due to specific client, state, or protocol requirements. Spike 10ml of sample with 50ul of Multi-analyte Stock solution (1000mg/L) section 10.5.

## 13.0 CALIBRATION AND STANDARDIZATION

13.1. Prepare standard 5-point curve by plotting instrument response against concentration values.

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 7 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

13.1.1. Generate a linear regression curve. Do not force through zero and do not average in the origin.

13.1.2. A calibration curve may be fitted to the calibration solution concentration/response data using the manufacturer's software.

13.1.3. Acceptance criteria for the calibration curve is a correlation coefficient (R value) $\geq$0.995. If the R-value is less than 0.995, the calibration standards must be remade and a new curve analyzed.

13.1.4. New calibration curves must be run every three months or if the instrument falls out of calibration whichever is sooner

13.2. Initial Calibration Verification Solution prepared from a different standard source is analyzed immediately after the calibration curve to verify the accuracy of the curve. The recovery of the ICV must be within 80-120%.

**14.0 PROCEDURE**

14.1. System Equilibrium:

14.1.1. Set up the ion chromatograph as specified in the manufacturer's instructions.

14.1.2 Turn on and prime the pump.

14.1.3 Adjust the eluent flow rate to 1.2 $\pm$ 0.1 ml/min. Adjust Regenerant pressure to 5PSI. Adjust restrictor at the end of the regenerant waste line to allow for 3-5ml/min. flow.

14.1.4 Allow the system to come to equilibrium (15-20 minutes). A stable baseline indicates system equilibrium.

14.2. Sample analysis:

14.2.1. For dirty samples filter sample through a pre-washed 0.2um pore diameter membrane filter. If sample is clean use 20um filter autosampler caps.

14.2.2. Fill autosampler vials with the sample to the fill line marked on the vial body (approximately 5 ml). Place vial cap into vial.

14.2.3. Place the filled vial into the sampler cassette and fully insert the cap using the insertion tool.

14.2.4. Place the filled cassettes into the automated sampler and start the run. Set sample run time to 64 minutes.

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 8 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

14.2.5. Check data for any needed dilutions and calculate percent recovery of check standards and sample spikes. Any data from samples that were diluted will have to be multiplied by the dilution factor before reporting.

14.3. Column cleanup procedure

14.3.1. Disconnect the suppressor from the analytical column. Reverse the order of the guard and analytical column in the eluent flow path. Double check that the eluent flows in the direction designated on each of the column labels.

14.3.1.1. CAUTION: When cleaning an analytical column and a guard column in series, ensure that the guard column is placed after the analytical column in the eluent flow path. Contaminants that have accumulated on the guard column can be eluted onto the analytical column and irreversibly damage it. If in doubt, clean each column separately.

14.3.2. Set the pump flow rate to 1.0 ml/min for the ICE-AS6 analytical.

14.3.3. Rinse the column for 15 minutes with reagent water before pumping the 0.1M oxalic acid over the column. Acetone can also be used to remove organics. Start with a 5% solution and increase up to 15%, but do not exceed 15%.

14.3.4. Pump the cleanup solution through the column for at least 60 minutes.

14.3.5. Rinse the column for 30 minutes with reagent water before pumping eluent over the column.

14.3.6. Equilibrate the columns with eluent before resuming normal operations for at least 30 minutes.

14.3.7. Reconnect the ASRS-Ultra to the analytical column.

14.4 Retention time (migration time) is the expected time retention time or migration time in minutes for the component. If the retention time is unknown, enter any number greater then zero. The correct retention time can be determined later from the first calibration run, and the component table then updated. In subsequent calibrations, PeakNet will automatically update the retention time. The Update Retention Time setting must be selected in the calibration Parameters dialog box.

## 15.0 CALCULATIONS

15.1. Using the computer and software packages, prepare a linear regression calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve.

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 9 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

The response factor produced from a linear equation best fits the detector's response. The equation used is shown below.

$$Y = K0 + K1 \times X$$

At least four points are needed to fit the equation: thus, the calibration must have at least four levels for all components.

The following values, used to calculate component amount, are determined automatically by the Method Editor and cannot be edited.

**X**= area
**K0** indicates the Y intercept of the calibration curve.
**K1** is the coefficient for the first-degree variable. When the fit type is linear, K1 indicates the slope of the calibration curve for the selected calibration level.

The equation for the calibration curve fit used to calculate the component amount is displayed at the bottom of the replicate page. The r2 value (Coefficient of Determination) for the component is shown at the bottom of the replicate page.

15.2. The analyst corrects the results for and dilution factors:

$$Xf = Xj * \text{Dilution Factor}$$

Where:
Xf = Final sample concentration
Xj = calculated concentration of sample at instrument

15.3. Report only those values that are less than the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

## 16.0 METHOD PERFORMANCE

16.1. The method detection limit (MDL) is to be performed every year in accordance with the specifications in 40 CFR 136, appendix B, and must demonstrate the ability to quantitate at or below the reporting limit for each acid. The current MDL is on file with the department supervisor and the QA Department.

## 17.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

17.1. Obtained ICV and CCV/LCS values must be within 80-120% of the true value.

17.2. Acceptance limits for sample spike recovery are based on the historical data and are statistically derived annually. They are maintained in the laboratory LIMs system. If the

lab calculated limits are wider than the method limits, the method limits of 80-120% are used for evaluation of sample spike acceptance.

17.3. Sample duplicates are required to have a calculated RPD $\leq$ 20.

17.4. ICB and CCB values must be less than the STL quantitation limit.

17.4.1. All blanks associated with USACE samples should be less than ½ the STL Buffalo quantitation limit for each anion.

## 18.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

18.1. If acceptance criteria are exceeded for any QC element, all related samples and check standards must be repeated.

## 19.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

19.1 If acceptable data can not be obtained, a Job Exception Form is to be filled out and turned in to the appropriate project manager in order to notify of the client.

19.2 Historical data review may be used to evaluate sample results.

## 20.0 WASTE MANAGEMENT/ POLLUTION PREVENTION

20.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for " Waste Management and Pollution Prevention."

20.2 Waste Streams Produced by the Method –The following waste streams are produced when this method is carried out.

20.2.1 Alkaline and/or acidic waste generated by the analysis. Dispose of this waste in the " A" waste container.

20.2.2 Contaminated plastic materials such as IC syringes, filters, caps and vials utilized for sample preparation. All plastic materials should be disposed of in the recycling containers located throughout the lab.

## 21.0 REFERENCE

21.1. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio, Revision 2.1, August 1993

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 11 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

21.2. Method 5560, Standard Methods for the Examination of Water and Wastewater, 20th Edition,

21.3. Dionex application note #45, "Fatty Acid Analysis"

**22.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA**

22.1. Analytical Run sequence

22.2. Wet Chemistry Batch Summary & Data Review Checklist

**23.0 CHANGES FROM PREVIOUS REVISION**

23.1 Changed the reporting limit of Butyric acid from 2 mg/L to 1 mg/L

23.2 Changed the concentration of the regenerant solution from 4 mM to 10 mM

23.3 Changed the concentration of the eluent solution from 0.6 mM to 1.0 mM

23.4 Removed MSD reference and added specific recipe for MS in section 12.6

23.5 Added 64 minute run time to section 14.2.4

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 12 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

**22.1 Analytical Run Sequence**

LCS/CCV
ICB
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
CCV
CCB
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample
Sample dup
Sample Spike
CCV
CCB

| SOP No. AWC-VFA-20 | Revision No. 1 | Date February 4, 2004 | Page 13 of 13 |
|---|---|---|---|

**TITLE: Volatile Fatty Acids**
**Supercedes: Revision 0**

## 22.2 Wet Chemistry Batch Summary & Data Review Summary

**WET CHEMISTRY BATCH SUMMARY**

Parameter _____ Method _____ Batch #_____

| Comment # | Comment |
|---|---|
| 1 | NA |
| 2 | Sample(s) was diluted for matrix interference. |
| 3 | Sample(s) was diluted for excessive foaming/ |
| 4 | Sample(s) was diluted for turbidity. |
| 5 | NA |
| 6 | NA |
| 7 | NA |
| 8 | Sample(s) was diluted for high concentration of target analyte |
| 9 | Sample(s) was diluted for turbidity. |
| 10 | Sample(s) was diluted for color. |
| 11 | There was insufficient volume for a lower dilution. |
| 12 | Sample(s) was diluted for viscosity. |
| 13 | Sample(s) was diluted for other reason (detail required) |
| 14 | Sample(s) required re-run to verify result. |
| 15 | Sample(s) requires re-run to verify deviation from historical result. |
| 16 | Sample(s) requires re-run for CCB failure. |
| 17 | Sample(s) affected by elevated CCB are greater than 10x detection limit. |
| 18 | Sample was colored. |
| 19 | Sample(s) was received outside of Holding Times. |
| 20 | Sample(s) contained a high amount of settleable material. |
| 21 | Sample(s) contained a high amount of suspended material. |
| 22 | Sample(s) were centrifuged for turbidity. |
| 23 | There was insufficient volume for analysis of sample at method required volume. |
| 24 | There was insufficient volume for re-analysis of the sample(s). |
| 25 | There was insufficient volume for dilution of the sample(s). |
| 26 | There was insufficient volume for Dup/Spk. |
| 27 | Sample(s) was cloudy |
| 28 | See accompanying Job Exception Report. |

Comments and Corrective actions

#_____ Sample(s)_____

#_____ Sample(s)_____

#_____ Sample(s)_____

#_____ Sample(s)_____

CCV/CCB Compliant? NA_____ YES_____ NO_____(see reason below)

Other_____

_____

_____

Technician _____ Date_____

2nd Review _____ Date_____ Number of Reanalysis for this batch:_____

Review _____ Date_____ WC Summary Rev 1 7-2003

| STL Edison Standard Operating Procedure | Revision Date: April 1, 2004 |
|---|---|
| Title: ORTHOPHOSPHATE, Analysis of Orthophosphate in Water<br>Laboratory Director: _____<br>Technical Director: _____<br>QA Manager: _____<br>Department Manager: _____<br>File Location: f:\qaqc\sops\nelac\nelac sops 2004\140wetch\general\opo4ww04.doc | SOP Number Opo4ww04<br>Revision 2<br>Page 1 of 8 |

UNCONTROLLED COPY

1. SCOPE AND APPLICATION

1.1. This SOP describes the procedure for analysis of ortho-phosphate using EPA Method 365.2 and SM 4500 P E. This method is applicable to ground water, wastewater and drinking water.

2. METHOD SUMMARY

2.1. A combined reagent added to the sample forms a blue complex proportional to the amount of ortho-phosphate present. Each time samples are analyzed, a method blank is analyzed. The results must be less than the reporting limit. The laboratory control sample must be recovered within manufacturer specified control limits. With each batch of samples a matrix spike and matrix spike duplicate are analyzed. The recovery and RPD must be within laboratory generated limits.

3. INTERFERENCES

3.1. High iron concentration can cause the precipitation of and subsequent loss of phosphorus.

3.2. Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than 0.l mg/l.

3.3. Hexavalent chromium and nitrite interfere to give low biased results if greater than 1 mg/l.

4. APPARATUS AND MATERIALS

4.1. Spectrophotometer, 880nm

4.2. pH Meter

4.3. Automatic pipets (Finnpipet and Oxford) with tips

4.4. Acid rinsed glassware

5. REAGENTS

5.1. Sulfuric Acid, conc.

5.2. Sodium hydroxide solution: 10 N Dissolve 400.0 g NaOH in deionized water and dilute to 1000 ml. Stable for 6 months.

5.3. Antimony potassium tartrate solution: Dissolve 1.37 g K(SbO) $C_4H_4O_6 \bullet 1/2H_2O$ in deionized water and dilute to 500 ml. Store refrigerated in an amber bottle. Stable for 6 months.

5.4. Ammonium molybdate solution: Dissolve 10 g of $(NH_4)_6 \cdot Mo_7O_{24}.4H_2O$ in deionized water and dilute to 250 ml. Store refrigerated in a plastic bottle no more than 6 months.

5.5. Ascorbic acid solution: Dissolve 4.40 g ascorbic acid in deionized water and dilute to 250 ml. Store refrigerated for one week.

5.6. Sulfuric acid, 5 N: Dilute 140 ml of conc. $H_2SO_4$ with deionized water to 1000 ml. Cool to room temperature with ice. Stable for 6 months.

5.7. Sulfuric acid, 11 N: Dissolve 310 ml of conc. $H_2SO_4$ per 1 L DI water. Cool with ice to room temperature. Stable for 6 months.

5.8. Combined Reagent: Place 250 ml of $5N.H_2SO_4$ in a 500-ml flask. Add 25 ml of tartrate solution. Swirl. Add 75 ml of molybdate solution. Swirl. Add 150 ml of ascorbic acid solution. Swirl. Stable for 4 hours.

6. STANDARDS

6.1. Stock Phosphorus solution, (50 mg/l): Dissolved 0.2197g $KH_2PO_4$ (dried at 105 °C) in deionized water and diluted to 1 liter.

6.2. Prepare standards in 50.0 ml volumetric flasks as indicated below:

| Standard (uls) | Concentration ug/l) |
| --- | --- |
| 0 | 0 |
| 30 | 30 |
| 50 | 50 |
| 100 | 100 |
| 200 | 200 |
| 500 | 500 |

7. PRESERVATION AND HANDLING

7.1. The holding time for orthophosphate is 48 hours.

7.2. Samples should be refrigerated at 4°C until the time of analysis.

8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

None

8.5. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
| --- | --- | --- | --- |
| Sodium Hydroxide | Corrosive | 2 Mg/M3-Ceiling | Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness. |
| Sulfuric Acid | Corrosive Oxidizer Dehydrator Poison Carcinogen | 1 Mg/M3-TWA | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

9. PROCEDURE

9.1. If samples have color or turbidity, a background correction must be made.

9.2. ALL GLASSWARE USED DURING THE PROCEDURE SHOULD BE RINSED FIRST WITH 11N $H_2SO_4$ OR COLOR INDICATOR AND THEN WITH DEIONIZED WATER BEFORE USE.

9.3. Allow color indicator to sit in cuvette for several minutes to develop color from any phosphorus on cuvette.

9.4. Place 50.0ml sample or standard into 100ml-specimen cup.

9.5. With pH paper check that pH is between 6 to 8. If not, adjust with $H_2SO_4$ or NaOH and note in logbook if there is a significant volume change (1 ml or greater).

9.6. Add 8.0ml of combined reagent. Allow sample to develop color for a total of 10 - 30 minutes. Read absorbance at 880 nm on

spectrophotometer. If sample develops color darker than highest standard make appropriate dilution to 50 ml and re-colorize.

9.7. If colorized sample looks turbid or if original sample has color, then pour 25 ml of sample into separate cup. Add two ml of 5 N $H_2SO_4$ to acidify and 2 ml of deionized water and read background. NOTE: For most samples a background is not necessary since acid from color indicator clears up turbidity or color in sample.

9.8. Data Processing:

9.8.1. Calculations:

9.8.1.1. Transfer absorbance and dilutions that were recorded in workbook into computer spreadsheet for ortho-phosphorus.

9.8.1.2. Subtract background absorbances where applicable.

9.8.1.3. Run linear regression. Verify correlation coefficient is greater than 0.997.

9.8.1.4. Print spreadsheet and curve. Record results in workbook.

9.8.2. Results:

9.8.2.1. Transfer results to analyte sheets. Attach copies of spreadsheets and copy of workbook and place in job folder. Sign chronicles.

9.8.2.2. Fill out and submit quality control sheets as required to manager.

9.8.2.3. Notify Wet Chemistry supervisor if quality control limits are exceeded.

10. QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed.

10.1.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water

and process through the entire analytical method. MDLs should be determined yearly.

10.2. Samples are separated into QA batches. This does not include the blank, matrix spike and matrix spike duplicate samples and Laboratory Control Sample. Open a quality control batch every two weeks or every 20 samples, whichever is first.

10.3. For each QA Batch the following procedures must be performed:

10.3.1. A blank must be analyzed each time samples are analyzed. Use deionized water for the blank. The results must be below the reporting limit.

10.3.2. A Laboratory Control Sample is performed daily and is obtained from an outside vendor. This measures method performance on the matrix being analyzed. The results must be within laboratory generated control limits.

10.3.3. Two portions of the same sample (matrix spike and matrix spike duplicate) are spiked. The recovery and relative percent difference must be within laboratory generated control limits. Calculate Recoveries and RPD as follows:

$$\% \text{ Recovery} = \frac{(\text{MS or MSD result} - \text{sample conc.}) \times 100}{\text{Amount spiked}}$$

$$\text{RPD} = \frac{2 \times (\text{ppm MS} - \text{ppm MSD}) \times 100}{(\text{ppm MS} + \text{ppm MSD})}$$

10.4. Instrument calibration should be verified in the following manner:

10.4.1. After initial calibration, every 10 samples and after last sample, a midpoint standard and blank will be analyzed. Verify ICV/CCV are 90-110% of value and ICB/CCB are below the reporting limit.

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated (flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective

actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

13. METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The

resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

15. REFERENCES

15.1 Methods for Chemical Analysis of Water and Wastes, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; Test Method 365.2.

15.2 Standard Methods for the Examination of Water and Wastewater , 18th Edition, American Public Health Association, Baltimore Maryland, 1992, SM 4500 P E.

| STL Edison Standard Operating Procedure | Revision Date: April 1, 2004 |
|---|---|
| Title: TKN, Analysis of Total Kjeldahl Nitrogen, Colorimetric, Semi-Automated Block Digester | SOP Number Tkn04 |
| Laboratory Director: | Revision 2 |
| Technical Director: | |
| QA Manager: | Page 1 of 11 |
| Department Manager: | |
| File Location: f:\qaqc\sops\nelac\nelac sops 2004\140wetch\general\tkn04.doc | |

UNCONTROLLED COPY

## 1. SCOPE AND APPLICATION

1.1. This SOP describes TKN analysis using EPA Method 351.2 and QuikChem Method 10-107-06-2-D with a semi-automated block digester. This method covers the determination of total kjeldahl nitrogen in drinking water, ground and surface water, solids, domestic and industrial waste.

1.2. The procedure converts the nitrogen components of biological origin such as amino acids, proteins, and peptides to ammonia but not the nitrogenous compounds of industrial wastes such as amines, nitro-compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines. The applicable range is 0.2 to 20 mgN/l TKN.

## 2. METHOD SUMMARY

2.1. The sample is heated in the presence of $H_2SO_4$, $K_2SO_4$, and $HgSO_4$ for four and one half hours. The residue is cooled, diluted and placed on the autoanalyzer for ammonia determination. This digested sample may also be used for phosphorus determination. Each time samples are digested a method blank and laboratory control sample are prepared and analyzed. The results of the method blank must be less than the reporting limit. The LCS must be recovered within manufacturer specified limits. A matrix spike and matrix spike duplicate are analyzed with each batch. The recovery and RPD must be within laboratory generated limits.

## 3. INTERFERENCES

3.1. Sample must not consume more than 10% of the sulfuric acid during digestion. The buffer will accommodate a range of 4.5 - 5.0% (v/v) $H_2SO_4$ in the diluted digestion sample with no change in signal intensity. The acid concentration affects the temperature of the sample in the digester. Too little acid and the temperature will be too

high, resulting in the loss of organic nitrogen. Too much acid and the temperature will be too low, resulting in an incomplete digestion.

3.2. High nitrate concentrations (10X or more than the TKN level) result in low TKN values. If nitrates are suspected, samples should be diluted and analyzed.

3.3. High concentration of organic matter may result in a high digester temperature and pyrolitic loss of nitrogen.

3.4. Digestates need to be free of turbidity.

4. APPARATUS AND MATERIALS

4.1. Lachat Quik Chem 8000 (autoanalyzer) with autosampler

4.2. TKN manifold with 1 channel

4.3. Lachat BD-46 Block Digester

4.4. Block digester tubes and cold fingers

4.5. Heating unit @ 60°C (650cm coil)

4.6. 5 ml and 20 ml Repipet Dispensers

4.7. Teflon Boiling Stones

4.8. Analytical balance

4.9. Vortex mixer

5. REAGENTS

5.1. Mercuric sulfate solution: Add 40.0 ml of DI water and 10 ml of conc. sulfuric acid into a 100-ml volumetric flask. Then add 8.0 g of red mercuric oxide (HgO). Dilute to mark and mix.

5.2. Digestion Solution: In a 1 L volumetric flask, add 133.0 g potassium sulfate ($K_2SO_4$) and 200 ml of conc. sulfuric acid to about 700 ml of DI water. Add 25 ml of mercuric sulfate solution. Dilute to mark and mix. Prepare fresh monthly.

5.3. Buffer: In a 1 L beaker, add 900 ml of DI water, 50 g potassium sodium tartrate, 50 g sodium hydroxide, and 26.8 g sodium phosphate dibasic heptahydrate ($Na_2HPO_4*7H20$). Stir until dissolved, then boil for 10 minutes. Cool to room temperature and transfer to a 1-L volumetric flask. Dilute to mark and mix.

5.4. 0.8 M NaOH: 32 g of NaOH in about 800 ml DI water. Dilute to mark and mix.

5.5. Salicylate nitroprusside: In a I L beaker, dissolve 150.0 g salicylic acid sodium salt and 1.00 g sodium nitroferricyanide dihydrate in about 800 ml of DI water. Transfer to a 1-L volumetric flask, dilute to mark and mix. Prepare fresh monthly.

5.6. Hypochlorite Solution: In a 250-ml volumetric flask, dilute 15.75 ml of 5.0% sodium hypochlorite (Clorox) with deionized water. Dilute to mark and mix. Prepare fresh daily.

5.7. Diluent: Dissolve 31.7 g potassium sulfate and 48 ml of conc. sulfuric acid in about 800 ml of DI water. Dilute to mark and mix. Prepare fresh weekly. Note: The diluent must match the digestion matrix.

6. STANDARDS

6.1. TKN Stock Solution: In a 1 L volumetric flask, dissolve 3.819 g ammonium chloride ($NH_4Cl$) that has been dried for 2 hours @ 110°C in about 800ml of DI water. Dilute to mark and mix.

6.2. Preparation of standards: Use Class A 100-ml volumetric flask and DI water to prepare standards. Preserve standards using 0.40 ml of 1:1 $H_2SO_4$ when preparing standards. Standards in digestion matrix is good for 28 days. Standards must be digested in the same manner as samples.

| TKN concentration (mgN/l) | Volume(ml of 1000 mgN/l TKN stock) |
| --- | --- |
| 20.0 | 2.0 |
| 15.0 | 1.5 |
| 10.0 | 1.0 |
| 5.0 | 0.5 |
| 1.0 | 0.10 |

| | |
| --- | --- |
| 0.20 | 1.0 of 20 mgN/L standard |
| 0.0 | 0.0 |

7. SAMPLE HANDLING AND PRESERVATION

7.1. Samples may be preserved by the addition of 2 ml of concentrated sulfuric acid per liter and stored at 4° C.

7.2. The holding time for TKN is 28 days.

8. SAFETY

8.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Sodium Nitroferricyanide will generate Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

Mercuric Oxide, Red may affect the central nervous system.

8.3 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
| --- | --- | --- | --- |

| | | | |
|---|---|---|---|
| Chloroform | Carcinogen Irritant | 50 ppm Ceiling | Acts as a relatively potent anesthetic. Irritates respiratory tract and causes central nervous system effects, including headache, drowsiness, dizziness. Causes skin irritation resulting in redness and pain. Removes natural oils. May be absorbed through skin. Vapors cause pain and irritation to eyes. Splashes may cause severe irritation and possible eye damage. |
| Mercuric Oxide, Red | Oxidizer Corrosive Poison | 0.1 Mg/M3 Ceiling (Mercury Compou nds) | Extremely toxicCauses irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage. |
| Sodium Hydroxide | Corrosive Poison | 2 ppm, 5 $mg/m^3$ | This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system. |
| Sodium Nitroferri-cyanide | Poison | 5 $mg/m^3$ as HCN gas | This material may cause irritation if it comes into the contact with the skin. The materials will give off HCN gas if combined with strong acids. Inhalation of HCN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death. |

| | | | |
|---|---|---|---|
| Sulfuric Acid | Corrosive Oxidizer Dehydrator Poison Carcinogen | 1 Mg/M3- TWA | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

9. PROCEDURE

9.1. Digestion:

9.1.1. Wash all glassware with 1:1 HCl to minimize contamination.

9.1.2. Set the temperature and time on block digester (Temp1 = 200 °C, Time1 = 60 min., Temp2 = 380 °C, Time2 = 210 min.). The typical ramp time is about 180 minutes. The total digestion time is 4 1/2 hours.

9.1.3. Preheat block digester @ 200 °C for about one hour.

9.1.4. Label digestion tubes. Include in the set: STDS, QA, blank, LCS, CCV, CCB, and samples. The QA batch consists of the sample, MS, MSD, LCS, and a Blank.

9.1.5. Pour 20 ml of standards/samples into proper digestion tubes for waters or 0.4g of solid and 20ml of deionized water.

9.1.6. Add 5 ml of Digestion Solution into digestion tubes and mix using a vortex mixer.

9.1.7. Add 10-12 Teflon boiling stones into digestion tube.

9.1.8. Place tubes in the preheated block digester and press start. Initial Temp 160 °C for 60 minutes. Samples should begin to boil off.

9.1.9. After one hour, place cold fingers on tubes. Set up controller to 380°C and continue digestion until the temperature is reached. Keep digesting for another ½ hour.

9.1.10. Remove digestion tubes from block digester and let cool under a hood for 5 - 10 minutes (Sulfuric Fumes).

9.1.11. Rapidly add 20 ml of deionized water into each tube and vortex to mix. Cover each tube with parafilm until samples are analyzed.

9.2. Instrumental Analysis

9.2.1. Follow manifold scheme of this method in the Lachat manual.

9.2.2. Turn on the heating unit @ 60 °C for 15 minutes before analysis.

9.2.3. Pump deionized water through reagent lines to check for leaks and smooth flow. NOTE: Add the buffer reagent on line first and pump for 5 minutes before adding other reagents. Once all lines are in place, pump 15 minutes more for the baseline to stabilize.

9.2.4. Set up the Tray Table with all appropriate QA checks. Run a CCV/CCB every 10 samples and at end of the run. The recovery must be 90 - 110 %.

9.2.5. Place standards and samples into the autosampler cup.

9.2.6. Run tray.

9.2.7. Make all appropriate dilutions to dilute samples below the highest standard.

9.2.8. The standard curve must have a correlation coefficient of 0.997 or greater.

Note: At the end of the analysis, run deionized water through all reagent lines FIRST, except the buffer line. Buffer line is the last line to switch to deionized water rinse. Air out all reagent lines.

9.3. Data Processing:

9.3.1. Calculations for Solids Samples:

$$\text{mg/Kg TKN} = \frac{A \times B}{C} \times D \div \frac{E}{100}$$

A = reading from instrument in mg/L
B = final volume after digestion
C = weight of sample in grams
D = dilution factor(if applicable)
E = % solid of sample

9.3.2. Record results in workbook and transfer to analyte sheet.

9.3.3. Place analyte sheets in job folders and sign chronicles.

9.3.4. Notify supervisor if quality control limits are exceeded.

9.3.5. Submit quality control sheets to manager as required for each batch.

10. QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed.

10.1.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water and process through the entire analytical method. MDLs should be determined yearly.

10.2. Samples are separated into QA batches. This does not include the blank, duplicate sample and Laboratory Control Sample. Open a quality control batch every two weeks or every 20 samples, whichever is first.

10.3. For each QA Batch the following procedures must be performed:

10.3.1. A blank must be analyzed each time samples are analyzed. Use deionized water for the blank. The results must be below the reporting limit.

10.3.2. A Laboratory Control Sample is obtained from an outside vendor and is used to measure method performance on the matrix being analyzed. The results must be within manufacturer specified limits.

10.3.3. Two portions of the same sample (matrix spike and matrix spike duplicate) are spiked with nitrogen. The recovery and relative percent difference must be within laboratory generated control limits. Calculate Recoveries and RPD as follows:

$$\% \text{ Recovery} = \frac{\text{MS(or MSD) result} - \text{sample conc.} \times 100}{\text{Amount spiked}}$$

$$\text{RPD} = \frac{2(\text{ppm MS} - \text{ppm MSD}) \times 100}{(\text{ppm MS} + \text{ppm MSD})}$$

10.4. Instrument calibration should be verified in the following manner:

10.4.1. The standard curve correlation coefficient must be greater than or equal to 0.997.

10.4.2. After initial calibration, every 10 samples and after last sample, a midpoint standard and blank will be analyzed. Verify ICV/CCV are 90-110% of value and ICB/CCB are below the reporting limit.

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLILNG OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated(flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

## 12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage.

13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the

Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 All MDL results are available on file.

14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

15. REFERENCES

15.1. Methods for Chemical Analysis of Water and Wastewaters, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; Test Method 351.2.

15.2. QuikChem Method 10-204-00-1-A, Determination of Kjeldahl Nitrogen in Waters.

| STL Edison Standard Operating Procedure | Revision Date: April 1, 2004 |
|---|---|
| Title: AMMONIA, Analysis of Ammonia in Water, Wastewater and Soil-Automated | SOP Number Nh3au04M |
| Laboratory Director: _____ | Revision 1 |
| Technical Director: _____ | Page 1 of 12 |
| QA Manager: _____ | |
| Department Manager: _____ | |
| File Location: f:\qaqc\sops\nelac\nelac sops 2004\140wetch\nitrogen\nh3au04m.doc | |

UNCONTROLLED COPY

1. SCOPE AND APPLICATION

1.1. Methods EPA 350.1, 350.2, SM 4500 NH3-B and QuikChem Method 10-107-06-1-C are described in this SOP. The SOP is applicable to the analysis of ammonia in waters, wastewaters, and soils.

1.2. The automated method has a detector that is sensitive to approximately 0.02 mg N/L as NH3.

2. METHOD SUMMARY

2.1. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue, which is proportional to the amount of ammonia. Each batch of twenty samples or less a matrix spike and matrix spike duplicate are distilled and analyzed. The results are compared to laboratory generated control limits. Each time samples are distilled a method blank and a blank spike sample are digested. The method blank must be less than the MDL.

3. INTERFERENCES

3.1. All samples must be distilled prior to analysis. Interferences are reduced or eliminated by using the distillation procedure.

3.2. Alkalinity over 500mg/L, acidity over 100mg/L interfere. These are removed by the distillation step.

3.3. Calcium and Magnesium ions in sufficient quantities can cause precipitation during analysis, this can be reduced by adding EDTA and sodium potassium tartrate.

3.4. Color, turbidity, and certain organic species may cause interference. Turbidity may be removed with manual filtration.

4. APPARATUS AND MATERIALS

4.1. EASY-Dist distillation apparatus

4.2. Boiling tube/stopper

4.3. Mini-Allihn condenser/condenser stem

4.4. Sloped T-joint

4.5. Graduated cylinder, 50 ml

4.6. Magnetic stirrer

4.7. Automatic pipettors or volumetric pipets

4.8. Class A volumetric flasks

4.9. pH meter

4.10. Micro-porous boiling stones

4.11. Size 19/22 clips

4.12. Flow injection analysis equipment designed to deliver a react sample and reagents in the required order and ratios.

4.12.1. Autosampler

4.12.2. Multichannel proportioning pump

4.12.3. Reaction Manifold

4.12.4. Colorimetric detector

4.12.5. Data System

4.12.6. Heating Unit

5. REAGENTS

5.1. Ammonia free water

5.2. Sodium Hydroxide, 15N: Dissolve 300g g of NaOH in 500ml of deionized water.

5.3. Sodium Hydroxide, 1M: Dissolve 40 g of NaOH in one liter of deionized water.

5.4. Borate Buffer: Dissolve 9.5g of sodium borate decahydrate (Na2B4O7*10H2O) in a 1L volumetric flask containing 800mls of deionized water. Add 88mls of 0.1 N NaOH and dilute to mark with deionzed water.

5.5. Boric Acid 2%: Dissolve 20 g of $H_3BO_3$ in a 1L volumetric flask containing 500ml of deionized water. Dilute to volume.

5.6. Sodium Phenolate: In a 1L volumetric flask, dissolve 83 g of crystalline phenol in approximately 600ml deionized water. While stirring, slowly add 32 g sodium hydroxide. Cool, dilute to mark, and invert three times.

5.7. Sodium Hypochlorite: In a 500ml volumetric flask, dilute 262.5 g of 5% sodium hypochlorite to the mark with deionized water.

5.8. Buffer: In 1 L volumetric flask, dissolve 50.0 g disodium ethylenediamine tetraacetate (Na2EDTA) and 5.5 g of Sodium hydroxide in about 900 ml of deionized water. Dilute to mark and invert three times.

5.9. Sodium Nitroprusside: In a 1L volumetric flask, dissolve 3.50 g sodium nitroprusside and dilute to mark with deionized water.

6. STANDARDS

6.1. Ammonia Stock Standard(1000mg N/L as NH3): In a 1L volumetric flask, dissolve 3.819g of ammonium chloride( NH4Cl) that has been dried for two hours at 110 deg C in about 800ml of deionized water. Dilute to mark and invert three times.

6.2. Initial Calibration Verification Standard-prepare as above from a secondary vendor.

7. PRESERVATION AND HANDLING

7.1. Samples must be preserved to a pH less than 2 with sulfuric acid upon sample collection.

7.2. Holding time for ammonia is 28 days.

8. SAFETY

8.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

8.2. Eye protection, lab coat and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

8.3. All questions pertaining to any safety procedure should be brought to the department manager or Edison Safety Officer.

8.4. SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

Sodium Nitroferricyanide will generate Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

8.5 PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

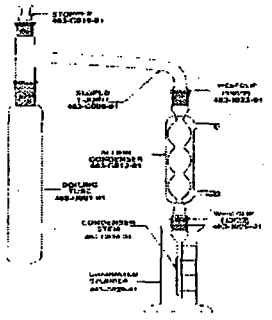
| Material (1) | Hazards | Exposure Limit (2) | Signs and symptoms of exposure |
| --- | --- | --- | --- |
| Phenol | Corrosive | 5 ppm-TWA | Breathing vapor, dust or mist results in digestive disturbances. Will irritate, possibly burn respiratory tract. Rapidly absorbed through the skin with systemic poisoning effects to follow. Discoloration and severe burns may occur, but may be disguised by a loss in pain sensation. Eye burns with redness, pain, blurred vision may occur. May cause severe damage and blindness. |

| | | | |
|---|---|---|---|
| Sodium Hydroxide | Corrosive | 2 Mg/M3-Ceiling | Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness. |
| Sodium Nitroferri-cyanide | Poison | 5 $mg/m^3$ as HCN gas | This material may cause irritation if it comes into the contact with the skin. The materials will give off HCN gas if combined with strong acids. Inhalation of HCN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death. |
| Sulfuric Acid | Corrosive Oxidizer Dehydrator Poison Carcinogen | 1 Mg/M3-TWA | Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness. |
| 1 – Always add acid to water to prevent violent reactions. | | | |
| 2 – Exposure limit refers to the OSHA regulatory exposure limit. | | | |

## 9. PROCEDURE

### 9.1. Cleaning Procedure for Distillation Glassware:

9.1.1. Boiling tubes must be treated prior to sample distillation. Add 25 ml of deionized water to the boiling tubes along with boiling chips treated with dilute NaOH. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.



9.2. Distillation Procedure:

9.2.1 *WATER SAMPLES*

9.2.1.1 To 40 ml of sample adjust the pH to 9.5 using 15 N NaOH and 1M NaOH.

9.2.1.2 Transfer the sample to the boiling tubes, add 2.5 ml of the borate buffer. Mix sample and check pH, readjust if needed.

9.2.1.3 Add 2-3 boiling stones and assemble distillation apparatus as shown in figure 1.

9.2.1.4 Place 5.0 ml of 2% Boric Acid solution and 2.0ml of deionized water in 50 ml cylinder.

9.2.1.5 Place condenser stem in the graduated cylinder, slide the cylinder and stem under condenser and connect stem to condenser with clip. **NOTE: Make sure the condenser tip is submerged in the Boric acid solution.** Turn on condenser water.

9.2.1.6 Heat the distillation apparatus to the following settings: Rate1: 15$^0$C/min; Temp1: 210$^0$C; Time1: 1.5Hour; Rate2: 0; Temp2: 210$^0$C; Time2: 0. ***Note***: Insulate glassware if needed, a single long sheet of aluminum foil around the exposed tube and T-joint glassware surfaces on each side is generally sufficient.

9.2.1.7 Collect 30 ml of distillate.

9.2.1.8 Discontinue heating. **REMOVE THE STOPPER FROM THE TOP OF THE T- JOINT WHILE COOLING** to prevent the collected distillate from being sucked back into the boiling tube.

9.2.1.9 Disconnect the stem from the condenser and remove the graduated cylinder from the apparatus.

9.2.1.10 Dilute the collected distillate to a final volume of 50 ml with deionized water.

*9.2.2 SEDIMENT/SOLID SAMPLES*

9.2.2.1 Weigh 1.0g or less of wet solid sample into a 100 ml beaker. Add 50 ml DI water. Adjust pH to 9.5 by adding 1N NaOH dropwise. Add 2.5 ml of borate buffer. Mix sample and check pH. Readjust final ph if necessary.

9.2.2.2 Proceed to section 9.2.1.3 and collect 30 ml of distillate. Dilute to 50 ml with deionized water.

9.3. Calibration Preparation:

9.3.1. Prepare calibration standards as shown in the chart below. Add the respective amount of Standard ammonium chloride solution to a 100ml volumetric flask containing 12.5ml of Boric Acid and dilute to a final volume of 100ml with deionized water.

| Volume (ul) of1000 mg N/L Stock | Conc. of NH3 (mg/L) |
| --- | --- |
| 1000ul | 10.0 |
| 400ul | 4.0 |
| 200ul | 2.0 |
| 100ul | 1.0 |
| 50ul | 0.5 |
| 1000ul of 10ppm | 0.1 |
| 0ul | 0.0 |

9.4. System Start-up:

9.4.1. Follow manifold scheme for this method.

9.4.2. Turn on heating unit at 60°C for 15 minutes before analysis.

9.4.3. Put all reagent lines into deionized water and turn the pump on. Check for leaks and slow flow rate.

9.4.4. Switch over reagent lines to proper reagent. Let reagent run through manifold for 15 minutes before analysis to allow baseline to stabilize.

9.5. Setup tray table with all appropriate QA checks. CCV/CCB every 10 samples and at the end of the run.

9.6. Place standards and samples into autosampler cups.

9.7. The following analytical run sequence must be used when analyzing ammonia using this SOP :

Calibration
AICV
ICB
10 Samples
ACCV1
CCB1
Repeat until complete
ACCV2
CCB2

9.8. Run tray.

9.9. Make appropriate dilutions, if necessary.

9.10. Correlation Coefficient of 0.997 or greater must be obtained.

9.11. Data Processing

9.11.1. Calculations:

9.11.1.1. mg/l of Ammonia-Nitrogen = the result in the mg/l column on Lachat printout

9.11.2. Results:

9.11.2.1. Record results from laboratory workbook onto analyte sheet. Express results as mg/l as N.

9.11.2.2. Place analyte sheets in job folder and sign chronicle sheets.

9.11.2.3. Submit quality control sheets as necessary to laboratory manager with spreadsheet.

10. QUALITY CONTROL

10.1. Prior to the analysis of any samples the following must be performed.

10.1.1. Method Detection Limit (MDL) -- MDLs must be established by taking seven replicate aliquots of the fortified reagent water and process through the entire analytical method. MDLs should be determined yearly.

10.2. Instrument calibration is verified in the following manner:

10.2.1. The curve must be verified by analyzing an Initial Calibration Verification(ICV) solution at the midpoint of the calibration range. The value obtained must not differ from the true value by more than 10%. If it does the problem must be corrected, the instrument recalibrated, and the ICV reanalyzed.

10.2.2. The validity of the calibration curve must be verified periodically during an analysis. A continuing Calibration Verification (CCV) must be analyzed following every ten sample analyses. "Samples" include matrix spike, matrix spike duplicate, laboratory blanks, Spike Blanks, and environmental samples. The value obtained for the CCV must not differ from the true value by more than 10%. If it does, the problem must be corrected and the previous ten samples reanalyzed following the last good calibration verification.

10.2.3. Following each calibration verification a calibration blank must be analyzed. The results of this analysis must fall below the reported detection limit

10.3. Water and soil samples are separated into QA batches. Samples can be put into a batch for up to two weeks after the initial date, that is the date the first sample was distilled. Up to 20 samples can be put in a batch. This does not include MS, MSD, blank, and a spike blank, and Laboratory Control sample.

10.4. For each QA Batch the following procedures must be performed:

10.4.1. Two portions of the same sample (matrix spike and matrix spike duplicate) are spiked with 50 ug of NH3. The recovery and relative percent difference must be within laboratory generated control limits. Calculate Recoveries and RPD as follows:

$$\% \text{ Recovery} = \frac{\text{MS(or MSD) result} - \text{conc. of sample}}{\text{Amount spiked}} \times 100$$

$$\text{RPD} = \frac{2(\text{ppm MS} - \text{ppm MSD})}{(\text{ppm MS} + \text{ppm MSD}} \times 100$$

10.4.2. A spike blank, from a separate source, must also be run for each QA batch. Spike this with the same amount (50 ug NH3) as the MS and MSD.The recovery must be within laboratory generated control limits.

10.4.3. A blank must be run for each distillation run. The results must be below the reporting limit.

11. CORRECTIVE ACTIONS AND CONTINGENCIES FOR HANDLILNG OUT-OF-CONTROL OR UNACCEPTABLE DATA

Data that fails to meet minimum acceptance criteria will be annotated(flagged)with qualifiers and/or appropriate narrative comments defining the nature of the outage. If applicable, a Corrective Action Report will be initiated in order to provide for investigation and follow-up. For further corrective actions and contingencies for handling out-of-control or unacceptable data see *"Out of Control Events Corrective Actions"* SOP.

12. WASTE MANAGEMENT AND POLLUTION PREVENTION

12.1. WASTE MANAGEMENT:

The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

12.2. POLLUTION PREVENTION:

12.2.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

12.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage

## 13.0 METHOD PERFORMANCE

13.1 A method detection Limit (MDL) study is performed annually for this analysis. The MDL study is conducted by taking seven replicate preparations of a low-concentration standard (approximately 2-5 times the estimated method detection limit) through all sample preparation steps and analysis for the specified analytical method. MDL values are calculated from the standard deviation of analytical results and the Students' t value for the number of replicate samples analyzed. The resulting calculated MDL values are evaluated by the Laboratory Manager and the QA Manager against criteria to determine their acceptability.

13.2 *All MDL results are available on file.*

## 14. DEFINITIONS

14.1 Refer to document DEFDOC-04 for definitions.

## 15. REFERENCES

15.1 Methods for Chemical Analysis of Water and Wastes, EMSL-Cincinnati, EPA/600/4-79-020, March 1983 and 1979; Test Methods – 350.1 AND 350.2

15.2 Standard Methods for the Examination of Water and Wastewater , 18th Edition, American Public Health Association, Baltimore Maryland, 1992, SM 4500-NH3 D.

15.3 QuikChem Method 10-107-06-1-C, Determination of Ammonia (Phenolate) in Potable and Surface Waters.

# APPENDIX B
# SOIL VAPOR AND INDOOR AIR SOP'S


Environmental
Engineers & Scientists

# U.S. ENVIRONMENTAL PROTECTION AGENCY (EPA). JANUARY 1999. COMPENDIUM METHOD TO-15

EPA/625/R-96/010b

# Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

## Second Edition

## Compendium Method TO-15

## Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

## Method TO-15
## Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), which was prepared under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, and Scott Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development, were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John O. Burckle, EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- Heidi Schultz, ERG, Lexington, MA
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

Author(s)

- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Michael W. Holdren, Battelle, Columbus, OH

Peer Reviewers

- Karen Oliver, ManTech, RTP, NC
- Jim Cheney, Corps of Engineers, Omaha, NB
- Elizabeth Almasi, Varian Chromatography Systems, Walnut Creek, CA
- Norm Kirshen, Varian Chromatography Systems, Walnut Creek, CA
- Richard Jesser, Graseby, Smyrna, GA
- Bill Taylor, Graseby, Smyrna, GA
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled it's production.

## DISCLAIMER

## METHOD TO-15

## Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

### TABLE OF CONTENTS

## TABLE OF CONTENTS (continued)

## METHOD TO-15

### Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

### 1. Scope

**1.1** This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than $10^{-1}$ Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2).*

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

**1.2** This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a $10^{-6}$ or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at $10^{-6}$ risk concentrations, the total risk may be significantly greater.

**1.3** This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

**1.4** Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how

to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

**1.5** Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

**1.6** Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

## 2. Summary of Method

**2.1** The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

**2.2** After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

**2.3** Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

**2.4** To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

**2.5** The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

## 3. Significance

**3.1** Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid

adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.

- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

**3.2** With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

## 4. Applicable Documents

### 4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis.*
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures.*
- **Method E355** *Practice for Gas Chromatography Terms and Relationships.*
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology).*

### 4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990,* U. S. Congress, Washington, D.C., November 1990.

## 5. Definitions

*[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]*

**5.1 Gauge** Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

**5.2 Absolute Pressure**—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

**5.3 Cryogen**—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid $CO_2$ (bp -79.5°C ).

**5.4 Dynamic Calibration**—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

**5.5 Dynamic Dilution**—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

**5.6 MS-SCAN**—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

**5.7 MS-SIM**—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

**5.8 Qualitative Accuracy**—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

**5.9 Quantitative Accuracy**—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

**5.10 Replicate Precision**—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

**5.11 Duplicate Precision**—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

**5.12 Audit Accuracy**—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

## 6. Interferences and Contamination

**6.1** Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

**6.2** Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

**6.2.1** Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

**6.2.2** Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

**6.2.3** Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

**6.2.4** Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

**6.2.5** In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

## 7. Apparatus and Reagents

*[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]*

### 7.1 Sampling Apparatus

*[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC) sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]*

**7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).**

**7.1.1.1 Sampling Inlet Line.** Stainless steel tubing to connect the sampler to the sample inlet.

**7.1.1.2 Sample Canister.** Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

**7.1.1.3 Stainless Steel Vacuum/Pressure Gauges.** Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

**7.1.1.4 Electronic Mass Flow Controller.** Capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

**7.1.1.5 Particulate Matter Filter.** 2-$\mu$m sintered stainless steel in-line filter.

**7.1.1.6 Electronic Timer**. For unattended sample collection.

**7.1.1.7 Solenoid Valve**. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

**7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings**. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

**7.1.1.9 Thermostatically Controlled Heater**. To maintain above ambient temperature inside insulated sampler enclosure.

**7.1.1.10 Heater Thermostat**. Automatically regulates heater temperature.

**7.1.1.11 Fan**. For cooling sampling system.

**7.1.1.12 Fan Thermostat**. Automatically regulates fan operation.

**7.1.1.13 Maximum-Minimum Thermometer**. Records highest and lowest temperatures during sampling period.

**7.1.1.14 Stainless Steel Shut-off Valve**. Leak free, for vacuum/pressure gauge.

**7.1.1.15 Auxiliary Vacuum Pump**. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

*[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]*

**7.1.1.16 Elapsed Time Meter**. Measures duration of sampling.

**7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve**. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

**7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).**

**7.1.2.1 Sample Pump**. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

*[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]*

**7.1.2.2 Other Supporting Materials**. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

**7.2 Analytical Apparatus**

**7.2.1 Sampling/Concentrator System (many commercial alternatives are available).**

**7.2.1.1 Electronic Mass Flow Controllers**. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

**7.2.1.2 Vacuum Pump**. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

**7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings**. Coated with fused silica to minimize active adsorption sites.

**7.2.1.4 Stainless Steel Cylinder Pressure Regulators**. Standard, two-stage cylinder regulators with pressure gauges.

**7.2.1.5 Gas Purifiers**. Used to remove organic impurities and moisture from gas streams.

**7.2.1.6 Six-port Gas Chromatographic Valve**. For routing sample and carrier gas flows.

**7.2.1.7 Multisorbent Concentrator**. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

**7.2.1.7.1**A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

**7.2.1.7.2**An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

**7.2.1.8 Cryogenic Concentrator**. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

**7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.**

**7.2.2.1 Gas Chromatograph**. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

**7.2.2.2 Chromatographic Columns**. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

**7.2.2.3 Mass Spectrometer**. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

**7.2.2.3.1Linear Quadrupole Technology**. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the

parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

**7.2.2.3.2Ion Trap Technology**. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

**7.2.2.4 GC/MS Interface**. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

**7.2.2.5 Data System**. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

**7.2.2.6 Off-line Data Storage Device**. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

### 7.3 Calibration System and Manifold Apparatus (see Figure 8)

**7.3.1 Calibration Manifold.** Stainless steel, glass, or high purity quartz manifold, (e.g.,1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

**7.3.2 Humidifier.** 500-mL impinger flask containing HPLC grade deionized water.

**7.3.3 Electronic Mass Flow Controllers.** One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

**7.3.4 Teflon Filter(s).** 47-mm Teflon® filter for particulate collection.

### 7.4 Reagents

**7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures.** Best source (see Section 9).

**7.4.2 Helium and Air.** Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

**7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide.** Used to cool secondary trap.

**7.4.4 Deionized Water.** High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

## 8. Collection of Samples in Canisters

### 8.1 Introduction

**8.1.1** Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

**8.1.2** Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

**8.1.3** EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

### 8.2 Sampling System Description

**8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].**

**8.2.1.1** In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

**8.2.1.2** With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

**8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].**

**8.2.2.1** Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

**8.2.2.2** In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

**8.2.3 All Samplers.**

**8.2.3.1** A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.
P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.
T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ mL/min}$$

**8.2.3.2** For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

**8.2.3.3** The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

**8.2.3.4** The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

**8.2.3.5** As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

**8.2.3.6** Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

### 8.3 Sampling Procedure

**8.3.1** The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

**8.3.2** A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

*[Note: The sampling system should be contained in an appropriate enclosure.]*

**8.3.3** Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

**8.3.4** After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

*[Note: The following discussion is related to Figure 1]*

**8.3.5** To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

*[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]*

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

*[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]*

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

**8.3.6** The sampler is turned off and the elapsed time meter is reset to 000.0.

*[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]*

**8.3.7** The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

**8.3.8** The canister valve and vacuum/pressure gauge valve are opened.

**8.3.9** Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

**8.3.10** The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

**8.3.11** The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

**8.3.12** After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

**8.3.13** At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to desired pressure.

*[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]*

Time of day and elapsed time meter readings are also recorded.

**8.3.14** The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

*[Note: For a pressurized system, the final flow may be measured directly.]*

The sampler is turned off.

**8.3.15** An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

### 8.4 Cleaning and Certification Program

#### 8.4.1 Canister Cleaning and Certification.

**8.4.1.1** All canisters must be clean and free of any contaminants before sample collection.

**8.4.1.2** All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

*[Note: The canister cleaning system in Figure 10 can be used for this task.]*

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

**8.4.1.3** A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

*[Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]*

Air released/evacuated from canisters should be diverted to a fume hood.

**8.4.1.4** The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

**8.4.1.5** The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

**8.4.1.6** At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

**8.4.1.7** The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

**8.4.1.8** As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

*[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].*

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

**8.4.2 Cleaning Sampling System Components.**

**8.4.2.1** Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

**8.4.2.2** The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

**8.4.2.3** Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

**8.4.3 Zero Air Certification.**

*[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.]*

**8.4.3.1** The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

**8.4.3.2** The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

**8.4.3.3** The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

*[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]*

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

**8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System**

**8.4.4.1** Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

**8.4.4.2** Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

**8.4.4.3** The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

**8.4.4.4** For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

**8.4.4.5** After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

**8.4.4.6** Sample the dynamic calibration gas stream with the sampling system.

**8.4.4.7** Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

**8.4.4.8** At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

**8.4.4.9** A recovery of between 90% and 110% is expected for all targeted VOCs.

**8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.**

**8.4.5.1** Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

**8.4.5.2** Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

## 9. GC/MS Analysis of Volatiles from Canisters

### 9.1 Introduction

**9.1.1** The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

**9.1.2** With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

**9.1.3** Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

**9.1.4** With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

## 9.2 Preparation of Standards

**9.2.1 Introduction.**

**9.2.1.1** When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

**9.2.1.2** The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

**9.2.1.3** Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

**9.2.2 Preparing Working Standards.**

**9.2.2.1 Instrument Performance Check Standard.** Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

**9.2.2.2 Calibration Standards.** Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

**9.2.2.3 Internal Standard Spiking Mixture.** Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-$d_5$, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

**9.2.3 Standard Preparation by Dynamic Dilution Technique.**

**9.2.3.1** Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

**9.2.3.2** Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})\ (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

**9.2.3.3** Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(1000\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

### 9.2.4 Standard Preparation by Static Dilution Bottle Technique

*[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]*

**9.2.4.1** The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

**9.2.4.2** The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

**9.2.4.3** The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

**9.2.4.4** The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

**9.2.4.5** Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

**9.2.4.6** Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

**9.2.4.7** The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: $V_a$ = Volume of liquid neat standard injected into the flask, µL.
$d$ = Density of the liquid neat standard, mg/µL.
$V_f$ = Volume of the flask, L.

**9.2.4.8** To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

*[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]*

### 9.2.5 Standard Preparation Procedure in High Pressure Cylinders

*[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]*

**9.2.5.1** The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

**9.2.5.2** An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

**9.2.5.3** Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

**9.2.5.4** The cylinder is pressurized to 1000 psig with zero nitrogen.

*[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]*

**9.2.5.5** The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

**9.2.5.6** If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

*[Note: Both values must be expressed in the same units.]*

**9.2.5.7** If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(mL)(d)}{MW}$$

where:
- V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
- n = Moles.
- R = Gas constant, 0.08206 L-atm/mole °K.
- T = 298°K (standard temperature).
- P = 1 standard pressure, 760 mm Hg (1 atm).
- mL = Volume of liquid injected, mL.
- d = Density of the neat standard, g/mL.
- MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by $10^9$ to obtain the component concentration in ppb units.

**9.2.6 Standard Preparation by Water Methods.**

*[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].*

**9.2.6.1** A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

**9.2.6.2** The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

*[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]*

**9.2.6.3** A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

**9.2.6.4** This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

**9.2.6.5** At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

**9.2.6.6** The canister is allowed to equilibrate overnight before use.

**9.2.6.7** A schematic of this approach is shown in Figure 14.

**9.2.7 Preparation of Standards by Permeation Tubes.**

**9.2.7.1** Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

**9.2.7.2** The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

**9.2.8 Storage of Standards.**

**9.2.8.1** Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

**9.2.8.2** It is imperative that a storage logbook be kept to document storage time.

## 10. GC/MS Operating Conditions

### 10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

**10.1.1 Sample Collection Conditions**

| Cryogenic Trap | Adsorbent Trap |
|---|---|

| | | | |
|---|---|---|---|
| Set point | -150°C | Set point | 27°C |
| Sample volume | - up to 100 mL | Sample volume | - up to 1,000 mL |
| Carrier gas purge flow | - none | Carrier gas purge flow | - selectable |

*[Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.]*

**10.1.2 Desorption Conditions**

| Cryogenic Trap | | Adsorbent Trap | |
|---|---|---|---|
| Desorb Temperature | 120°C | Desorb Temperature | Variable |
| Desorb Flow Rate | ~ 3 mL/min He | Desorb Flow Rate | ~3 mL/min He |
| Desorb Time | <60 sec | Desorb Time | <60 sec |

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

**10.1.3 Trap Reconditioning Conditions.**

| Cryogenic Trap | | Adsorbent Trap | |
|---|---|---|---|
| Initial bakeout | 120°C (24 hrs) | Initial bakeout | Variable (24 hrs) |
| After each run | 120°C (5 min) | After each run | Variable (5 min) |

**10.2 GC/MS System**

**10.2.1** Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

**10.2.2** The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 μm film thickness fused silica column with refocusing on the column.

| Item | Condition | |
|---|---|---|
| Carrier Gas: | Helium | |
| Flow Rate: | Generally 1-3 mL/min as recommended by manufacturer | |
| Temperature Program: | Initial Temperature: | -50°C |
| | Initial Hold Time: | 2 min |
| | Ramp Rate: | 8° C/min |
| | Final Temperature: | 200°C |
| | Final Hold Time: | Until all target compounds elute. |

**10.2.3** The following are the recommended mass spectrometer conditions:

| Item | Condition |
|---|---|

| | |
|---|---|
| Electron Energy: | 70 Volts (nominal) |
| Mass Range: | 35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here. |
| Scan Time: | To give at least 10 scans per peak, not to exceed 1 second per scan]. |

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

### 10.3 Analytical Sequence

**10.3.1 Introduction.** The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤20 field samples.

### 10.4 Instrument Performance Check

**10.4.1 Summary.** It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

**10.4.2 Frequency.** Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

**10.4.3 Procedure.** The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

**10.4.4 Technical Acceptance Criteria.** Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

**10.4.5 Corrective Action.** If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

**10.4.6 Documentation.** Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

**10.5 Initial Calibration**

**10.5.1 Summary.** Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

**10.5.2 Frequency.** Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

**10.5.3 Procedure.** Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

**10.5.4 Calculations.**

*[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]*

**10.5.4.1 Relative Response Factor (RRF).** Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

where: RRF = Relative response factor.
$A_x$ = Area of the primary ion for the compound to be measured, counts.
$A_{is}$ = Area of the primary ion for the internal standard, counts.
$C_{is}$ = Concentration of internal standard spiking mixture, ppbv.
$C_x$ = Concentration of the compound in the calibration standard, ppbv.

*[Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. $C_{is}$ and $C_x$ must be in the same units.]*

**10.5.4.2 Mean Relative Response Factor.** Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

where: $\overline{RRF}$ = Mean relative response factor.
$x_i$ = RRF of the compound at concentration i.
n = Number of concentration values, in this case 5.

**10.5.4.3 Percent Relative Standard Deviation (%RSD).** Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: $SD_{RRF}$ = Standard deviation of initial response factors (per compound).
$RRF_i$ = Relative response factor at a concentration level i.
$\overline{RRF}$ = Mean of initial relative response factors (per compound).

**10.5.4.4 Relative Retention Times (RRT).** Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: $RT_c$ = Retention time of the target compound, seconds
$RT_{is}$ = Retention time of the internal standard, seconds.

**10.5.4.5 Mean of the Relative Retention Times ($\overline{RRT}$).** Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

where: $\overline{RRT}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

**10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard.** Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

**10.5.4.7 Mean Area Response ($\overline{Y}$) for Internal Standard.** Calculate the mean area response ($\overline{Y}$) for each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where: $\overline{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

**10.5.4.8 Mean Retention Times ($\overline{RT}$).** Calculate the mean of the retention times ($\overline{RT}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where: $\overline{RT}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

**10.5.5 Technical Acceptance Criteria for the Initial Calibration.**

**10.5.5.1** The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

*[Note: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.]*

**10.5.5.2** The RRT for each target compound at each calibration level must be withiin 0.06 RRT units of the mean RRT for the compound.

**10.5.5.3** The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

**10.5.5.4** The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

**10.5.6 Corrective Action.**

**10.5.6.1 Criteria.** If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

**10.5.6.2 Schedule.** Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

### 10.6 Daily Calibration

**10.6.1 Summary.** Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

**10.6.2 Frequency.** A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

**10.6.3 Procedure.** The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

**10.6.4 Calculations.** Perform the following calculations.

*[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]*

**10.6.4.1 Relative Response Factor (RRF).** Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

**10.6.4.2 Percent Difference (%D).** Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where: $RRF_c$ = RRF of the compound in the continuing calibration standard.

$\overline{RRF_i}$ = Mean RRF of the compound in the most recent initial calibration.

**10.6.5 Technical Acceptance Criteria.** The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

**10.6.6 Corrective Action.** If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

### 10.7 Blank Analyses

**10.7.1 Summary.** To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank

using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

**10.7.2 Frequency**. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

**10.7.3 Procedure**. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

**10.7.4 Calculations**. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

**10.7.5 Technical Acceptance Criteria**. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

**10.7.6 Corrective Action**. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

### 10.8 Sample Analysis

**10.8.1 Summary**. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

*[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary*

*in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]*

**10.8.2 Frequency.** If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

**10.8.3 Procedure for Instrumental Analysis.** Perform the following procedure for analysis.

**10.8.3.1** All canister samples should be at temperature equilibrium with the laboratory.

**10.8.3.2** Check and adjust the mass flow controllers to provide correct flow rates for the system.

**10.8.3.3** Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

**10.8.3.4** Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

**10.8.3.5** Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

**10.8.3.6** After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

**10.8.3.7** Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

**10.8.3.8** Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

**10.8.3.9** Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

**10.8.4 Calculations.** The equation below is used for calculating concentrations.

$$C_x = \frac{A_x C_{is} DF}{A_{is} \overline{RRF}}$$

where: $C_x$ = Compound concentration, ppbv.

$A_x$ = Area of the characteristic ion for the compound to be measured, counts.

$A_{is}$ = Area of the characteristic ion for the specific internal standard, counts.

$C_{is}$ = Concentration of the internal standard spiking mixture, ppbv

$\overline{RRF}$ = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

*[Note: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]*

**10.8.5 Technical Acceptance Criteria.**

*[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]*

**10.8.5.1** The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

**10.8.5.2** The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

**10.8.5.3** All of the target analyte peaks should be within the initial calibration range.

**10.8.5.4** The retention time for each internal standard must be within ±0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

**10.8.6 Corrective Action.** If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

*[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]*

**10.8.6.1** Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

**10.8.6.2** If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and

corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

**10.8.6.3** If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

## 11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

### 11.1 Introduction

**11.1.1** There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

**11.1.2** Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

**11.1.3** Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

### 11.2 Method Detection Limit

**11.2.1** The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

**11.2.2** The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

### 11.3 Replicate Precision

**11.3.1** The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where:

$x_1$ = First measurement value.

$x_2$ = Second measurement value.

$\bar{x}$ = Average of the two values.

**11.3.2** There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

### 11.4 Audit Accuracy

**11.4.1** A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

**11.4.2** Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

## 12. References

1. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14A, Second Edition,* U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/625/R-96/010b, January 1997.

2. Winberry, W. T., Jr., et al., *Statement-of-Work (SOW) for the Analysis of Air Toxics From Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Contract Laboratory Program, Washington, D.C., Draft Report, June 1990.

3. Coutant, R.W., *Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters*, U. S. Environmental Protection Agency, EPA Contract No. 68-DO-0007, Work Assignment No. 45, Subtask 2, Battelle, Columbus, OH, June 1993.

4. Kelly, T.J., Mukund, R., Gordon, S.M., and Hays, M.J., *Ambient Measurement Methods and Properties of the 189 Title III Hazardous Air Pollutants*, U. S. Environmental Protection Agency, EPA Contract No. 68-DO-0007, Work Assignment 44, Battelle, Columbus, OH, March 1994.

5. Kelly T. J. and Holdren, M.W., "Applicability of Canisters for Sample Storage in the Determination of Hazardous Air Pollutants," *Atmos. Environ.*, Vol. 29, 2595-2608, May 1995.

6. Kelly, T.J., Callahan, P.J., Pleil, J.K., and Evans, G.E., "Method Development and Field Measurements for Polar Volatile Organic Compounds in Ambient Air," *Environ. Sci. Technol.*, Vol. 27, 1146-1153, 1993.

7. McClenny, W.A., Oliver, K.D. and Daughtrey, E.H.., Jr. "Dry Purging of Solid Adsorbent Traps to Remove Water Vapor Before Thermal Desorption of Trace Organic Gases," *J. Air and Waste Manag. Assoc.,* Vol. 45, 792-800, June 1995.

8. Whitaker, D.A., Fortmann, R.C. and Lindstrom, A.B. "Development and Testing of a Whole Air Sampler for Measurement of Personal Exposures to Volatile Organic Compounds," *Journal of Exposure Analysis and Environmental Epidemiology*, Vol. 5, No. 1, 89-100, January 1995.

9. Pleil, J.D. and Lindstrom, A.B., "Collection of a Single Alveolar Exhaled Breath for Volatile Organic Compound Analysis," *American Journal of Industrial Medicine*, Vol. 28, 109-121, 1995.

10. Pleil, J.D. and McClenny, W.A., "Spatially Resolved Monitoring for Volatile Organic Compounds Using Remote Sector Sampling," *Atmos. Environ.,* Vol. 27A, No. 5, 739-747, August 1993.

11. Holdren, M.W., et al., Unpublished Final Report, EPA Contract 68-DO-0007, Battelle, Columbus, OH. Available from J.D. Pleil, MD-44, U. S. Environmental Protection Agency, Research Triangle Park, NC, 27711, 919-541-4680.

12. Morris, C.M., Burkley, R.E. and Bumgarner, J.E., "Preparation of Multicomponent Volatile Organic Standards Using Dilution Bottles," *Anal. Letts.*, Vol. 16 (A20), 1585-1593, 1983.

13. Pollack, A.J., Holdren, M.W., "Multi-Adsorbent Preconcentration and Gas Chromatographic Analysis of Air Toxics With an Automated Collection/Analytical System," in the *Proceedings of the 1990 EPA/A&WMA International Symposium of Measurement of Toxic and Related Air Pollutants*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA/600/9-90-026, May 1990.

14. Stephenson, J.H.M., Allen, F., Slagle, T., "Analysis of Volatile Organics in Air via Water Methods" in *Proceedings of the 1990 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/9-90-026, May 1990.

15. Oliver, K. D., Adams, J. R., Davehtrey, E. H., Jr., McClenny, W. A., Young, M. J., and Parade, M. A., "Techniques for Monitoring Toxices VOCs in Air: Sorbent Preconcentration Closed-Cycle Cooler Cryofocusing, and GC/MS Analysis," *Environ. Sci. Technol.*, Vol. 30, 1938-1945, 1996.

## APPENDIX A.

## LISTING OF SOME COMMERCIAL WATER MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

## APPENDIX B.

## COMMENT ON CANISTER CLEANING PROCEDURES

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

## APPENDIX C.

## LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF SPECIALLY-PREPARED CANISTERS

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

## APPENDIX D.

## LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

**TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs**

| Compound | CAS Nos | BP (°C) | V.P. (mmHg) | MW | TO-14A | CLP-SOW |
|---|---|---|---|---|---|---|
| Methyl chloride (chloromethane); CH3Cl | 74-87-3 | -23.7 | 3.8 x 10 | 50.5 | X | X |
| Carbonyl sulfide; COS | 463-58-1 | -50.0 | 3.7 x 10 | 60.1 | | |
| Vinyl chloride (chloroethene); C2H3Cl | 75-01-4 | -14.0 | 3.2 x 10 | 62.5 | X | X |
| Diazomethane; CH2N2 | 334-88-3 | -23.0 | 2.8 x 10 | 42.1 | | |
| Formaldehyde; CH2O | 50-00-0 | -19.5 | 2.7 x 10 | 30 | | |
| 1,3-Butadiene; C4H6 | 106-99-0 | -4.5 | 2.0 x 10 | 54 | | X |
| Methyl bromide (bromomethane); CH3Br | 74-83-9 | 3.6 | 1.8 x 10 | 94.9 | X | X |
| Phosgene; CCl2O | 75-44-5 | 8.2 | 1.2 x 10 | 99 | | |
| Vinyl bromide (bromoethene); C2H3Br | 593-60-2 | 15.8 | 1.1 x 10 | 107 | | |
| Ethylene oxide; C2H4O | 75-21-8 | 10.7 | 1.1 x 10 | 44 | | |
| Ethyl chloride (chloroethane); C2H5Cl | 75-00-3 | 12.5 | 1.0 x 10 | 64.5 | X | X |
| Acetaldehyde (ethanal); C2H4O | 75-07-0 | 21.0 | 952 | 44 | | |
| Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2 | 75-35-4 | 31.7 | 500 | 97 | X | X |
| Propylene oxide; C3H6O | 75-56-9 | 34.2 | 445 | 58 | | |
| Methyl iodide (iodomethane); CH3I | 74-88-4 | 42.4 | 400 | 141.9 | | |
| Methylene chloride; CH2Cl2 | 75-09-2 | 40.0 | 349 | 84.9 | X | X |
| Methyl isocyanate; C2H3NO | 624-83-9 | 59.6 | 348 | 57.1 | | |
| Allyl chloride (3-chloropropene); C3H5Cl | 107-05-1 | 44.5 | 340 | 76.5 | X | X |
| Carbon disulfide; CS2 | 75-15-0 | 46.5 | 260 | 76 | | |
| Methyl tert-butyl ether; C5H12O | 1634-04-4 | 55.2 | 249 | 86 | | |
| Propionaldehyde; C2H5CHO | 123-38-6 | 49.0 | 235 | 58.1 | | |
| Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2 | 75-34-3 | 57.0 | 230 | 99 | X | |

**TABLE 1. (continued)**

| Compound | CAS No. | BP (°C) | VP (mmHg) | MW | TO-14A | CLP-SOW |
|---|---|---|---|---|---|---|
| *Chloroprene (2-chloro-1,3-butadiene); C4H5Cl* | *126-99-8* | *59.4* | *226* | *88.5* | | |
| Chloromethyl methyl ether; C2H5ClO | 107-30-2 | 59.0 | 224 | 80.5 | | |
| Acrolein (2-propenal); C3H4O | 107-02-8 | 52.5 | 220 | 56 | | X |
| 1,2-Epoxybutane (1,2-butylene oxide); C4H8O | 106-88-7 | 63.0 | 163 | 72 | | |
| Chloroform; CHCl3 | 67-66-3 | 61.2 | 160 | 119 | X | X |
| Ethyleneimine (aziridine); C2H5N | 151-56-4 | 56 | 160.0 | 43 | | |
| 1,1-Dimethylhydrazine; C2H8N2 | 57-14-7 | 63 | 157.0 | 60.0 | | |
| Hexane; C6H14 | 110-54-3 | 69.0 | 120 | 86.2 | X | |
| 1,2-Propyleneimine (2-methylaziridine); C3H7N | 75-55-8 | 66.0 | 112 | 57.1 | | |
| Acrylonitrile (2-propenenitrile); C3H3N | 107-13-1 | 77.3 | 100 | 53 | X | |
| Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3 | 71-55-6 | 74.1 | 100 | 133.4 | X | X |
| Methanol; CH4O | 67-56-1 | 65.0 | 92.0 | 32 | | X |
| Carbon tetrachloride; CCl4 | 56-23-5 | 76.7 | 90.0 | 153.8 | X | X |
| Vinyl acetate; C4H6O2 | 108-05-4 | 72.2 | 83.0 | 86 | | X |
| Methyl ethyl ketone (2-butanone); C4H8O | 78-93-3 | 79.6 | 77.5 | 72 | | X |
| Benzene; C6H6 | 71-43-2 | 80.1 | 76.0 | 78 | X | X |
| Acetonitrile (cyanomethane); C2H3N | 75-05-8 | 82 | 74.0 | 41.0 | | X |
| Ethylene dichloride (1,2-dichloroethane); C2H4Cl2 | 107-06-2 | 83.5 | 61.5 | 99 | X | X |
| Triethylamine; C6H15N | 121-44-8 | 89.5 | 54.0 | 101.2 | | |
| Methylhydrazine; CH6N2 | 60-34-4 | 87. 8 | 49.6 | 46.1 | | |
| Propylene dichloride (1,2-dichloropropane); C3H6Cl2 | 78-87-5 | 97.0 | 42.0 | 113 | X | X |
| 2,2,4-Trimethyl pentane C8H18 | 540-84-1 | 99.2 | 40.6 | 114 | | |
| 1,4-Dioxane (1,4-Diethylene oxide); C4H8O2 | 123-91-1 | 101 | 37.0 | 88 | | |
| Bis(chloromethyl) ether; C2H4Cl2O | 542-88-1 | 104 | 30.0 | 115 | | |
| Ethyl acrylate; C5H8O2 | 140-88-5 | 100 | 29.3 | 100 | | |
| Methyl methacrylate; C5H8O2 | 80-62-6 | 101 | 28.0 | 100.1 | | |

**TABLE 1. (continued)**

| Compound | CAS No. | BP (°C) | V.P. (mmHg) | MW | TO-14A | CLP-SOW |
|---|---|---|---|---|---|---|
| Methyl methacrylate; C5H8O2 | 80-62-101 | 101 | 28.0 | 100.1 | | |
| 1,3-Dichloropropene; C3H4Cl2 (cis) | 542-75-6 | 112 | 27.8 | 111 | X | X |
| Toluene; C7H8 | 108-88-3 | 111 | 22.0 | 92 | X | X |
| Trichloroethylene; C2HCl3 | 79-01-6 | 87.0 | 20.0 | 131.4 | X | X |
| 1,1,2-Trichloroethane; C2H3Cl3 | 79-00-5 | 114 | 19.0 | 133.4 | X | X |
| Tetrachloroethylene; C2Cl4 | 127-18-4 | 121 | 14.0 | 165.8 | X | X |
| Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO | 106-89-8 | 117 | 12.0 | 92.5 | | |
| Ethylene dibromide (1,2-dibromoethane); C2H4Br2 | 106-93-4 | 132 | 11.0 | 187.9 | X | X |
| N-Nitroso-N-methylurea; C2H5N3O2 | 684-93-5 | 124 | 10.0 | 103 | | |
| 2-Nitropropane; C3H7NO2 | 79-46-9 | 120 | 10.0 | 89 | | |
| Chlorobenzene; C6H5Cl | 108-90-7 | 132 | 8.8 | 112.6 | X | X |
| Ethylbenzene; C8H10 | 100-41-4 | 136 | 7.0 | 106 | X | X |
| Xylenes (isomer & mixtures); C8H10 | 1330-20-7 | 142 | 6.7 | 106.2 | X | X |
| Styrene; C8H8 | 100-42-5 | 145 | 6.6 | 104 | X | X |
| p-Xylene; C8H10 | 106-42-3 | 138 | 6.5 | 106.2 | X | X |
| m-Xylene; C8H10 | 108-38-3 | 139 | 6.0 | 106.2 | X | X |
| Methyl isobutyl ketone (hexone); C6H12O | 108-10-1 | 117 | 6.0 | 100.2 | | |
| Bromoform (tribromomethane); CHBr3 | 75-25-2 | 149 | 5.6 | 252.8 | | |
| 1,1,2,2-Tetrachloroethane; C2H2Cl4 | 79-34-5 | 146 | 5.0 | 167.9 | X | X |
| o-Xylene; C8H10 | 95-47-6 | 144 | 5.0 | 106.2 | X | X |
| Dimethylcarbamyl chloride; C3H6ClNO | 79-44-7 | 166 | 4.9 | 107.6 | | |
| N-Nitrosodimethylamine; C2H6N2O | 62-75-9 | 152 | 3.7 | 74 | | |
| Beta-Propiolactone; C3H4O2 | 57-57-8 | Decomposes at 162 | 3.4 | 72 | | |
| Cumene (isopropylbenzene); C9H12 | 98-82-8 | 153 | 3.2 | 120 | | |

**TABLE 1. (continued)**

| Compound | CAS No. | BP (°C) | P° (mmHg) | MW | TO-14A | CLP-SOW |
|---|---|---|---|---|---|---|
| Cumene (isopropylbenzene); C9H12 | 98-82-8 | 153 | 3.2 | 120 | | |
| Acrylic acid; C3H4O2 | 79-10-7 | 141 | 3.2 | 72 | | |
| N,N-Dimethylformamide; C3H7NO | 68-12-2 | 153 | 2.7 | 73 | | |
| 1,3-Propane sultone; C3H6O3S | 1120-71-4 | 180/30mm | 2.0 | 122.1 | | |
| Acetophenone; C8H8O | 98-86-2 | 202 | 1.0 | 120 | | |
| Dimethyl sulfate; C2H6O4S | 77-78-1 | 188 | 1.0 | 126.1 | | |
| Benzyl chloride (a-chlorotoluene); C7H7Cl | 100-44-7 | 179 | 1.0 | 126.6 | X | X |
| 1,2-Dibromo-3-chloropropane; C3H5Br2Cl | 96-12-8 | 196 | 0.80 | 236.4 | | |
| Bis(2-Chloroethyl)ether; C4H8Cl2O | 111-44-4 | 178 | 0.71 | 143 | | |
| Chloroacetic acid; C2H3ClO2 | 79-11-8 | 189 | 0.69 | 94.5 | | |
| Aniline (aminobenzene); C6H7N | 62-53-3 | 184 | 0.67 | 93 | | |
| 1,4-Dichlorobenzene (p-); C6H4Cl2 | 106-46-7 | 173 | 0.60 | 147 | X | X |
| Ethyl carbamate (urethane); C3H7NO2 | 51-79-6 | 183 | 0.54 | 89 | | |
| Acrylamide; C3H5NO | 79-06-1 | 125/25 mm | 0.53 | 71 | | |
| N,N-Dimethylaniline; C8H11N | 121-69-7 | 192 | 0.50 | 121 | | |
| Hexachloroethane; C2Cl6 | 67-72-1 | Sublimes at 186 | 0.40 | 236.7 | | |
| Hexachlorobutadiene; C4Cl6 | 87-68-3 | 215 | 0.40 | 260.8 | X | X |
| Isophorone; C9H14O | 78-59-1 | 215 | 0.38 | 138.2 | | |
| N-Nitrosomorpholine; C4H8N2O2 | 59-89-2 | 225 | 0.32 | 116.1 | | |
| Styrene oxide; C8H8O | 96-09-3 | 194 | 0.30 | 120.2 | | |
| Diethyl sulfate; C4H10O4S | 64-67-5 | 208 | 0.29 | 154 | | |
| Cresylic acid (cresol isomer mixture);C7H8O | 1319-77-3 | 202 | 0.26 | 108 | | |
| o-Cresol; C7H8O | 95-48-7 | 191 | 0.24 | 108 | | |
| Catechol (o-hydroxyphenol); C6H6O2 | 120-80-9 | 240 | 0.22 | 110 | | |
| Phenol; C6H6O | 108-95-2 | 182 | 0.20 | 94 | | |

**TABLE 1. (continued)**

| Compound | CAS No. | BP (°C) | v.p. (mmHg)[1] | MW | TO-14A | CLP-SOW |
|---|---|---|---|---|---|---|
| Catechol (o-hydroxyphenol); C6H6O2 | 120-80-9 | 240 | 0.22 | 110 | | |
| Phenol; C6H6O | 108-95-2 | 182 | 0.20 | 94 | | |
| 1,2,4-Trichlorobenzene; C6H3Cl3 | 120-82-1 | 213 | 0.18 | 181.5 | X | X |
| nitrobenzene C6H5NO2 | 98-95-3 | 211 | 0.15 | 123 | | |

[1]Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:
(a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;
(b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
(c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

## TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS

| Compound | CAS No. | Primary Ion | Secondary Ion |
|---|---|---|---|
| Methyl chloride (chloromethane); CH3Cl | 74-87-3 | 50 | 52 |
| Carbonyl sulfide; COS | 463-S8-1 | 60 | 62 |
| Vinyl chloride (chloroethene); C2H3Cl | 7S-01-4 | 62 | 64 |
| Diazomethane; CH2N2 | 334-88-3 | 42 | 41 |
| Formaldehyde; CH2O | 50-00-0 | 29 | 30 |
| 1,3-Butadiene; C4H6 | 106-99-0 | 39 | 54 |
| Methyl bromide (bromomethane); CH3Br | 74-83-9 | 94 | 96 |
| Phosgene; CCl2O | 75-44-5 | 63 | 65 |
| Vinyl bromide (bromoethene); C2H3Br | 593-60-2 | 106 | 108 |
| Ethylene oxide; C2H4O | 75-21-8 | 29 | 44 |
| Ethyl chloride (chloroethane); C2H5Cl | 75-00-3 | 64 | 66 |
| Acetaldehyde (ethanal); C2H4O | 75-07-0 | 44 | 29, 43 |
| Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2 | 75-35-4 | 61 | 96 |
| Propylene oxide; C3H6O | 75-56-9 | 58 | 57 |
| Methyl iodide (iodomethane); CH3I | 74-88-4 | 142 | 127 |
| Methylene chloride; CH2Cl2 | 75-09-2 | 49 | 84, 86 |
| Methyl isocyanate; C2H3NO | 624-83-9 | 57 | 56 |
| Allyl chloride (3-chloropropene); C3H5Cl | 107-05-1 | 76 | 41, 78 |
| Carbon disulfide; CS2 | 75-15-0 | 76 | 44, 78 |
| Methyl tert-butyl ether; C5H12O | 1634-04-4 | 73 | 41, 53 |
| Propionaldehyde; C2H5CHO | 123-38-6 | 58 | 29, 57 |
| Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2 | 75-34-3 | 63 | 65, 27 |
| Chloroprene (2-chloro-1,3-butadiene); C4H5Cl | 126-99-8 | 88 | 53, 90 |
| Chloromethyl methyl ether; C2H5ClO | 107-30-2 | 45 | 29, 49 |
| Acrolein (2-propenal); C3H4O | 107-02-8 | 56 | 55 |
| 1,2-Epoxybutane (1,2-butylene oxide); C4H8O | 106-88-7 | 42 | 41, 72 |
| Chloroform; CHCl3 | 67-66-3 | 83 | 85, 47 |
| Ethyleneimine (aziridine); C2H5N | 151-56-4 | 42 | 43 |
| 1,1-Dimethylhydrazine; C2H8N2 | 57-14-7 | 60 | 45, 59 |
| Hexane; C6H14 | 110-54-3 | 57 | 41, 43 |
| 1,2-Propyleneimine (2-methylazindine); C3H7N | 75-55-8 | 56 | 57, 42 |
| Acrylonitrile (2-propenenitrile); C3H3N | 107-13-1 | 53 | 52 |
| Methyl chloroform (1,1,1 trichloroethane); C2H3Cl3 | 71-55-6 | 97 | 99, 61 |
| Methanol; CH4O | 67-56-1 | 31 | 29 |
| Carbon tetrachloride; CCl4 | 56-23-5 | 117 | 119 |
| Vinyl acetate; C4H6O2 | 108-05-4 | 43 | 86 |
| Methyl ethyl ketone (2-butanone); C4H8O | 78-93-3 | 43 | 72 |

**TABLE 2. (continued)**

| Compound | CAS No. | Primary Ion | Secondary Ion |
|---|---|---|---|
| Benzene; C6H6 | 71-43-2 | 78 | 77,50 |
| Acetonitrile (cyanomethane); C2H3N | 75-05-8 | 41 | 40 |
| Ethylene dichloride (1,2-dichloroethane); C2H4Cl2 | 107-06-2 | 62 | 64, 27 |
| Triethylamine; C6H15N | 121-44-8 | 86 | 58, 101 |
| Methylhydrazine; CH6N2 | 60-34-4 | 46 | 31, 45 |
| Propylene dichloride (1,2-dichloropropane); C3H6Cl2 | 78-87-5 | 63 | 41, 62 |
| 2,2,4-Trimethyl pentane; C8H18 | 540-84-1 | 57 | 41, 56 |
| 1,4-Dioxane (1,4 Diethylene oxide); C4H8O2 | 123-91-1 | 88 | 58 |
| Bis(chloromethyl) ether; C2H4Cl2O | 542-88-1 | 79 | 49, 81 |
| Ethyl acrylate; C5H8O2 | 140-88-5 | 55 | 73 |
| Methyl methacrylate; C5H8O2 | 80-62-6 | 41 | 69, 100 |
| 1,3-Dichloropropene; C3H4Cl2 (cis) | 542-75-6 | 75 | 39, 77 |
| Toluene; C7H8 | 108-88-3 | 91 | 92 |
| Trichloethylene; C2HCl3 | 79-01-6 | 130 | 132, 95 |
| 1,1,2-Trichloroethane; C2H3Cl3 | 79-00-5 | 97 | 83, 61 |
| Tetrachloroethylene; C2Cl4 | 127-18-4 | 166 | 164, 131 |
| Epichlorohydrin (l-chloro-2,3-epoxy propane); C3H5ClO | 106-89-8 | 57 | 49, 62 |
| Ethylene dibromide (1,2-dibromoethane); C2H4Br2 | 106-93-4 | 107 | 109 |
| N-Nitrso-N-methylurea; C2H5N3O2 | 684-93-5 | 60 | 44, 103 |
| 2-Nitropropane; C3H7NO2 | 79-46-9 | 43 | 41 |
| Chlorobenzene; C6H5Cl | 108-90-7 | 112 | 77, 114 |
| Ethylbenzene; C8H10 | 100-41-4 | 91 | 106 |
| Xylenes (isomer & mixtures); C8H10 | 1330-20-7 | 91 | 106 |
| Styrene; C8H8 | 100-42-5 | 104 | 78, 103 |
| p-Xylene; C8H10 | 106-42-3 | 91 | 106 |
| m-Xylene; C8H10 | 108-38-3 | 91 | 106 |
| Methyl isobutyl ketone (hexone); C6H12O | 108-10-1 | 43 | 58, 100 |
| Bromoform (tribromomethane); CHBr3 | 75-25-2 | 173 | 171, 175 |
| 1,1,2,2-Tetrachloroethane; C2H2Cl4 | 79-34-5 | 83 | 85 |
| o-Xylene; C8H10 | 95-47-6 | 91 | 106 |
| Dimethylcarbamyl chloride; C3H6ClNO | 79-44-7 | 72 | 107 |
| N-Nitrosodimethylamine; C2H6N2O | 62-75-9 | 74 | 42 |
| Beta-Propiolactone; C3H4O2 | 57-57-8 | 42 | 43 |
| Cumene (isopropylbenzene); C9H12 | 98-82-8 | 105 | 120 |
| Acrylic acid; C3H4O2 | 79-10-7 | 72 | 45, 55 |
| N,N-Dimethylformamide; C3H7NO | 68-12-2 | 73 | 42, 44 |
| 1,3-Propane sultone; C3H6O3S | 1120-71-4 | 58 | 65, 122 |

**TABLE 2. (continued)**

| Compound | CAS No. | Primary Ion | Secondary Ion |
|---|---|---|---|
| Acetophenone; C8H8O | 98-86-2 | 105 | 77,120 |
| Dimethyl sulfate; C2H6O4S | 77-78-1 | 95 | 66,96 |
| Benzyl chloride (a-chlorotoluene); C7H7Cl | 100-44-7 | 91 | 126 |
| 1,2-Dibromo-3-chloropropane; C3H5Br2Cl | 96-12-8 | 57 | 155, 157 |
| Bis(2-Chloroethyl)ether; C4H8Cl2O | 111-44-4 | 93 | 63, 95 |
| Chloroacetic acid; C2H3ClO2 | 79-11-8 | 50 | 45, 60 |
| Aniline (aminobenzene); C6H7N | 62-53-3 | 93 | 66 |
| 1,4-Dichlorobenzene (p-); C6H4Cl2 | 106-46-7 | 146 | 148, 111 |
| Ethyl carbamate (urethane); C3H7NO2 | 51-79-6 | 31 | 44, 62 |
| Acrylamide; C3H5NO | 79-06-1 | 44 | 55, 71 |
| N,N-Dimethylaniline; C8H11N | 121-69-7 | 120 | 77, 121 |
| Hexachloroethane; C2Cl6 | 67-72-1 | 201 | 199, 203 |
| Hexachlorobutadiene; C4Cl6 | 87-68-3 | 225 | 227, 223 |
| Isophorone; C9H14O | 78-59-1 | 82 | 138 |
| N-Nitrosomorpholine; C4H8N2O2 | 59-89-2 | 56 | 86, 116 |
| Styrene oxide; C8H8O | 96-09-3 | 91 | 120 |
| Diethyl sulfate; C4H10O4S | 64-67-5 | 45 | 59, 139 |
| Cresylic acid (cresol isomer mixture); C7H8O | 1319-77-3 | | |
| o-Cresol; C7H8O | 95-48-7 | 108 | 107 |
| Catechol (o-hydroxyphenol); C6H6O2 | 120-80-9 | 110 | 64 |
| Phenol; C6H6O | 108-95-2 | 94 | 66 |
| 1,2,4-Trichlorobenzene; C6H3Cl3 | 120-82-1 | 180 | 182, 184 |
| Nitrobenzene; C6H5NO2 | 98-95-3 | 77 | 51, 123 |

**TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA**

| Mass | Ion Abundance Criteria |
|---|---|
| 50 | 8.0 to 40.0 Percent of m/e 95 |
| 75 | 30.0 to 66.0 Percent of m/e 95 |
| 95 | Base Peak, 100 Percent Relative Abundance |
| 96 | 5.0 to 9.0 Percent of m/e 95 (See note) |
| 173 | Less than 2.0 Percent of m/e 174 |
| 174 | 50.0 to 120.0 Percent of m/e 95 |
| 175 | 4.0 to 9.0 Percent of m/e 174 |
| 176 | 93.0 to 101.0 Percent of m/e 174 |
| 177 | 5.0 to 9.0 Percent of m/e 176 |

[1]All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

| TO-14A List | Lab #1 SCAN | Lab #2 SIM |
|---|---|---|
| Benzene | 0.34 | 0.29 |
| Benzyl Chloride | – | – |
| Carbon tetrachloride | 0.42 | 0.15 |
| Chlorobenzene | 0.34 | 0.02 |
| Chloroform | 0.25 | 0.07 |
| 1,3-Dichlorobenzene | 0.36 | 0.07 |
| 1,2-Dibromoethane | – | 0.05 |
| 1,4-Dichlorobenzene | 0.70 | 0.12 |
| 1,2-Dichlorobenzene | 0.44 | – |
| 1,1-Dichloroethane | 0.27 | 0.05 |
| 1,2-Dichloroethane | 0.24 | – |
| 1,1-Dichloroethene | – | 0.22 |
| cis-1,2-Dichloroethene | – | 0.06 |
| Methylene chloride | 1.38 | 0.84 |
| 1,2-Dichloropropane | 0.21 | – |
| cis-1,3-Dichloropropene | 0.36 | – |
| trans-1,3-Dichloropropene | 0.22 | – |
| Ethylbenzene | 0.27 | 0.05 |
| Chloroethane | 0.19 | – |
| Trichlorofluoromethane | – | – |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | | – |
| 1,2-Dichloro-1,1,2,2-tetrafluoroethane | – | – |
| Dichlorodifluoromethane | – | – |
| Hexachlorobutadiene | – | – |
| Bromomethane | 0.53 | – |
| Chloromethane | 0.40 | – |
| Styrene | 1.64 | 0.06 |
| 1,1,2,2-Tetrachloroethane | 0.28 | 0.09 |
| Tetrachloroethene | 0.75 | 0.10 |
| Toluene | 0.99 | 0.20 |
| 1,2,4-Trichlorobenzene | – | – |
| 1,1,1-Trichloroethane | 0.62 | 0.21 |
| 1,1,2-Trichloroethane | 0.50 | – |
| Trichloroethene | 0.45 | 0.07 |
| 1,2,4-Trimethylbenzene | – | – |
| 1,3,5-Trimethylbenzene | – | – |
| Vinyl Chloride | 0.33 | 0.48 |
| m,p-Xylene | 0.76 | 0.08 |
| o-Xylene | 0.57 | 0.28 |

[1]Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

## TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP) FROM EPA NETWORK OPERATIONS[1]

| Monitoring Compound Identification | EPA's Urban Air Toxics Monitoring Program (UATMP) | | | EPA's Toxics Air Monitoring Stations (TAMS) | | |
|---|---|---|---|---|---|---|
| | %RP | # | ppbv | %RP | # | ppbv |
| Dichlorodifluoromethane | -- | | -- | 13.9 | 47 | 0.9 |
| Methylene chloride | 16.3 | 07 | 4.3 | 19.4 | 47 | 0.6 |
| 1,2-Dichloroethane | 36.2 | 31 | 1.6 | -- | -- | -- |
| 1,1,1-Trichloroethane | 14.1 | 44 | 1.0 | 10.6 | 47 | 2.0 |
| Benzene | 12.3 | 56 | 1.6 | 4.4 | 47 | 1.5 |
| Trichloroethene | 12.8 | 08 | 1.3 | -- | -- | -- |
| Toluene | 14.7 | 76 | 3.1 | 3.4 | 47 | 3.1 |
| Tetrachloroethene | 36.2 | 12 | 0.8 | -- | -- | -- |
| Chlorobenzene | 20.3 | 21 | 0.9 | -- | -- | -- |
| Ethylbenzene | 14.6 | 32 | 0.7 | 5.4 | 47 | 0.5 |
| m-Xylene | 14.7 | 75 | 4.0 | 5.3 | 47 | 1.5 |
| Styrene | 22.8 | 59[2] | 1.1 | 8.7 | 47 | 0.2[2] |
| o-Xylene | -- | | -- | 6.0 | 47 | 0.5 |
| p-Xylene | -- | | | | | |
| 1,3-Dichlorobenzene | 49.1 | 06 | 0.6 | -- | -- | -- |
| 1,4-Dichlorobenzene | 14.7 | 14 | 6.5 | -- | -- | -- |

[1]Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.
[2]Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

## TABLE 6. AUDIT ACCURACY (AA) VALUES[1] FOR SELECTED COMPENDIUM METHOD TO-14A COMPOUNDS

| Selected Compounds From TO-14A List | FY-88 TAMS AA(%), N=30 | FY-88 UATMP AA(%), N=3 |
|---|---|---|
| Vinyl chloride | 4.6 | 17.9 |
| Bromomethane | -- | 6.4 |
| Trichlorofluoromethane | 6.4 | -- |
| Methylene chloride | 8.6 | 31.4 |
| Chloroform | -- | 4.2 |
| 1,2-Dichloroethane | 6.8 | 11.4 |
| 1,1,1-Trichloroethane | 18.6 | 11.3 |
| Benzene | 10.3 | 10.1 |
| Carbon tetrachloride | 12.4 | 9.4 |
| 1,2-Dichloropropane | -- | 6.2 |
| Trichloroethene | 8.8 | 5.2 |
| Toluene | 8.3 | 12.5 |
| Tetrachloroethene | 6.2 | -- |
| Chlorobenzene | 10.5 | 11.7 |
| Ethylbenzene | 12.4 | 12.4 |
| o-Xylene | 16.2 | 21.2 |

[1]Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

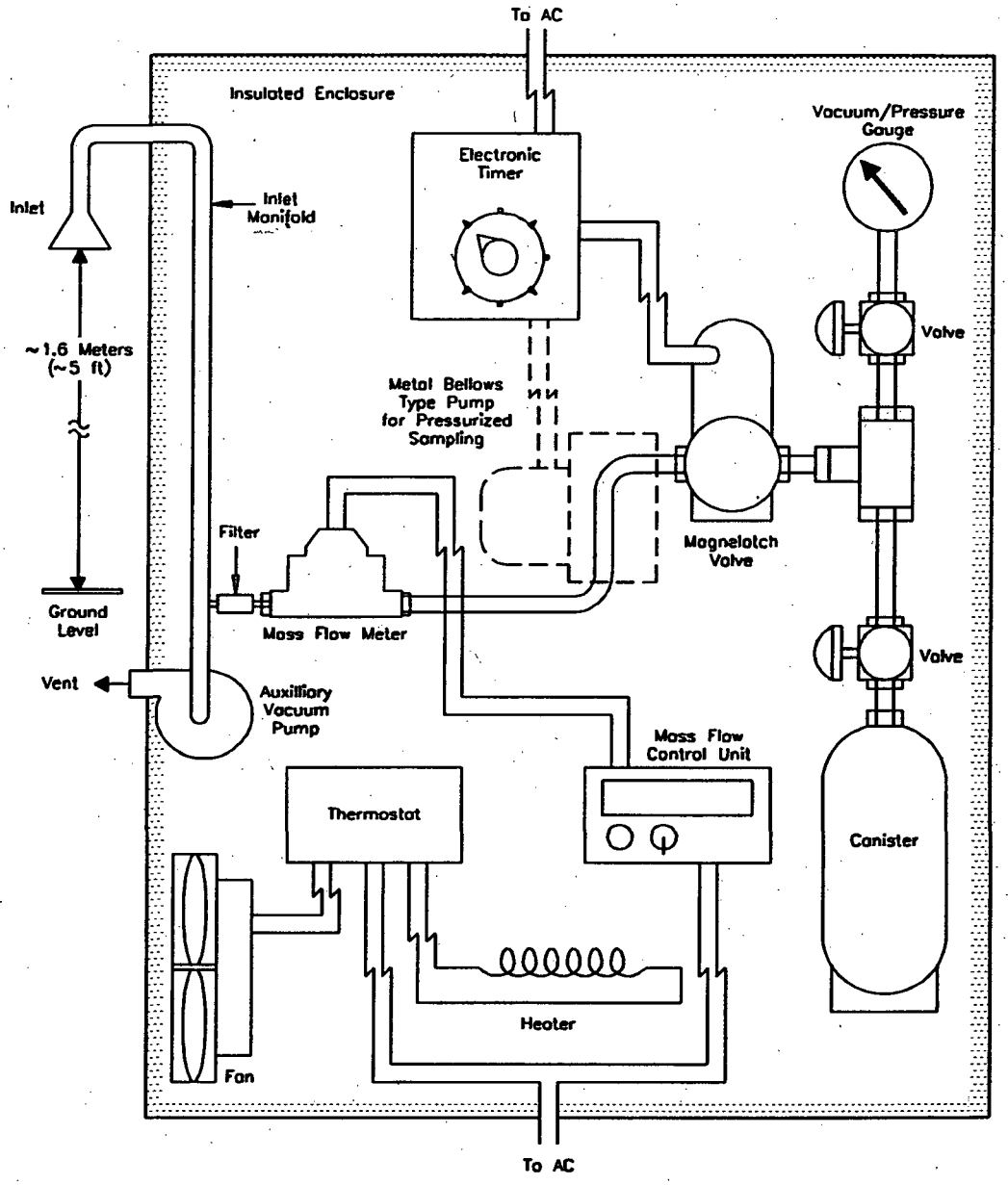
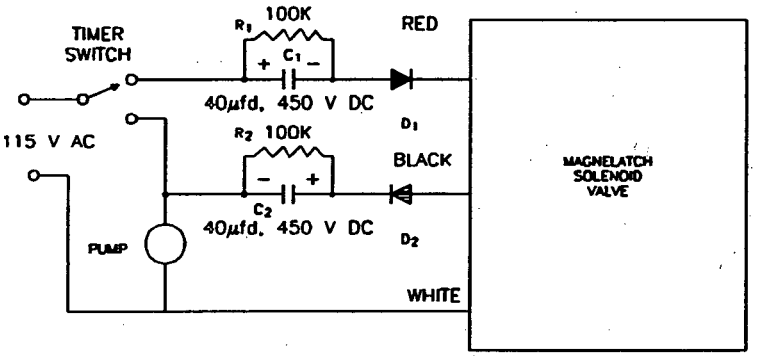


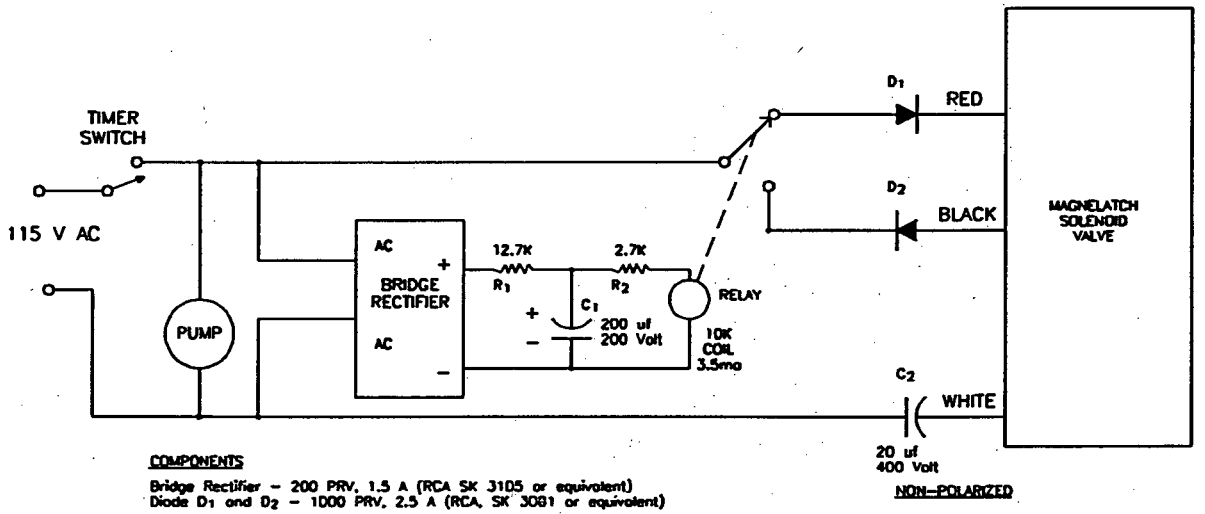

Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.




COMPONENTS

Capacitor $C_1$ and $C_2$ – 40 uf, 450 VDC (Sprague Atom TVA 1712 or equivalent)
Resister $R_1$ and $R_2$ – 0.5 watt, 5% tolerance
Diode $D_1$ and $D_2$ – 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

(a). Simple Circuit for Operating Magnelatch Valve




COMPONENTS

Bridge Rectifier – 200 PRV, 1.5 A (RCA SK 3105 or equivalent)
Diode $D_1$ and $D_2$ – 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
Capacitor $C_1$ – 200 uf, 250 VDC (Sprague Atom TVA 1528 or equivalent)
Capacitor $C_2$ – 20 uf, 400 VDC Non-Polarized (Sprague Atom TVAN 1652 or equivalent)
Relay – 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resistor $R_1$ and $R_2$ – 0.5 watt, 5% tolerance

(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

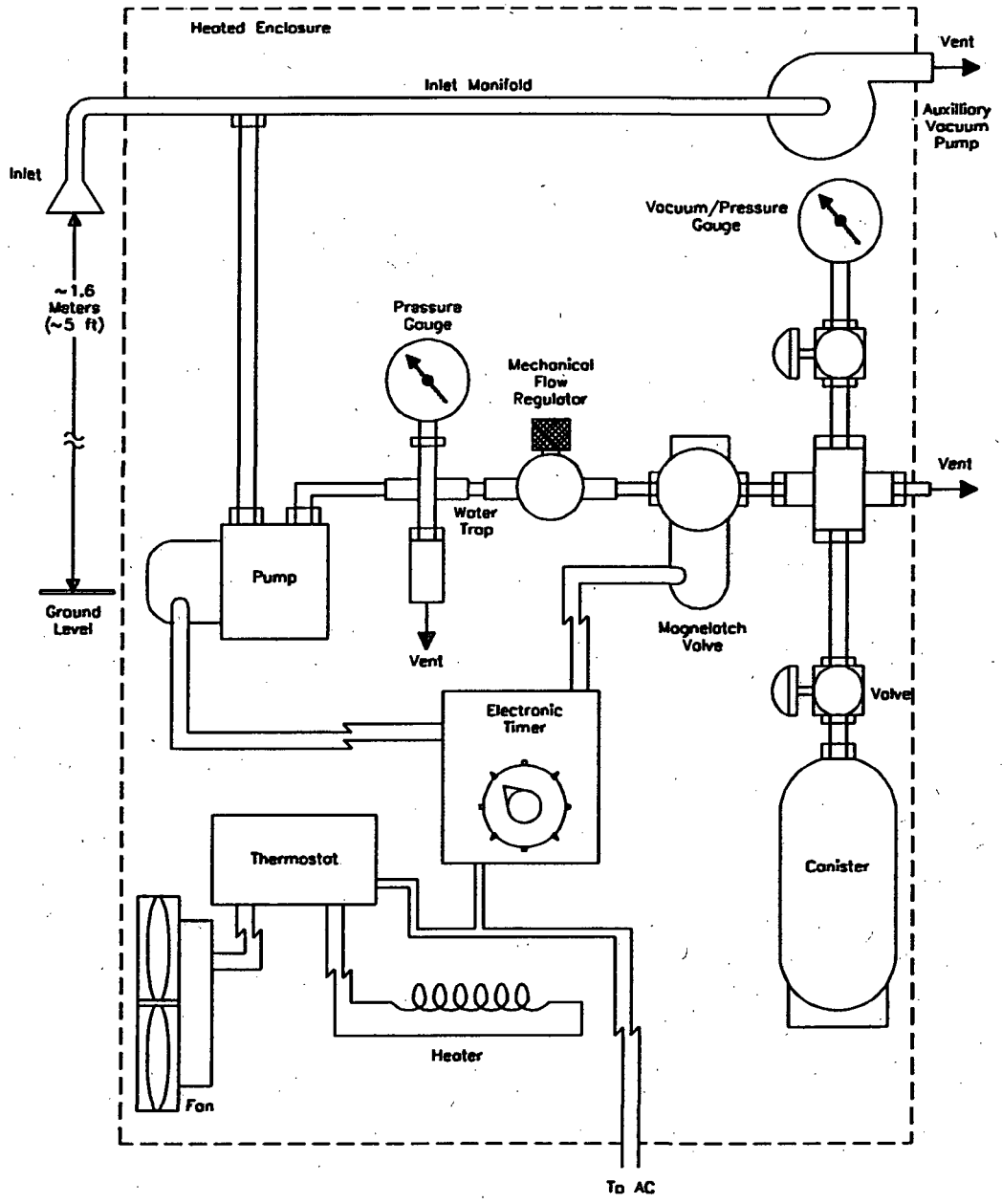



Figure 3. Alternative sampler configuration for pressurized canister sampling.

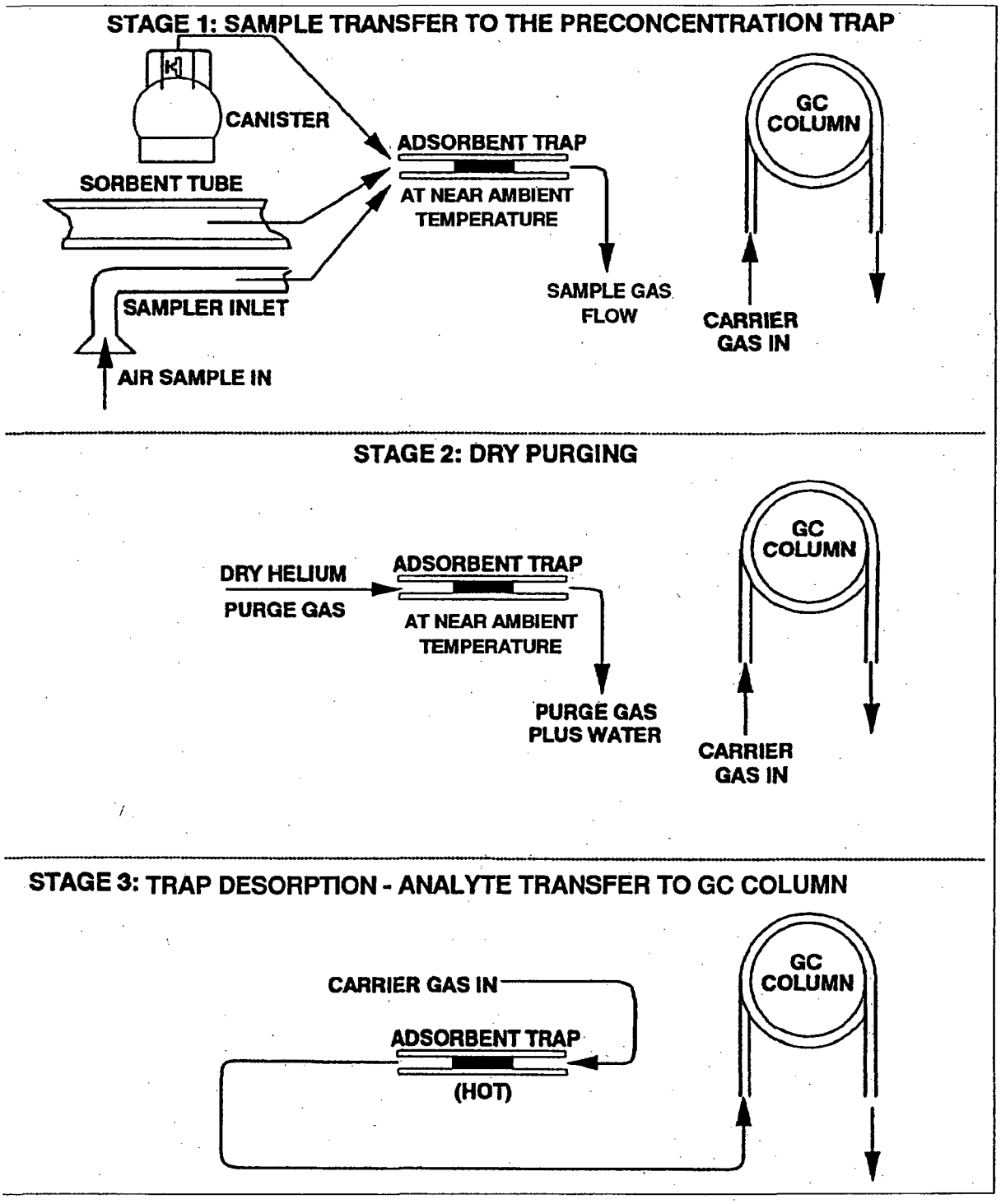



Figure 4. Illustration of three stages of dry purging of adsorbent trap.

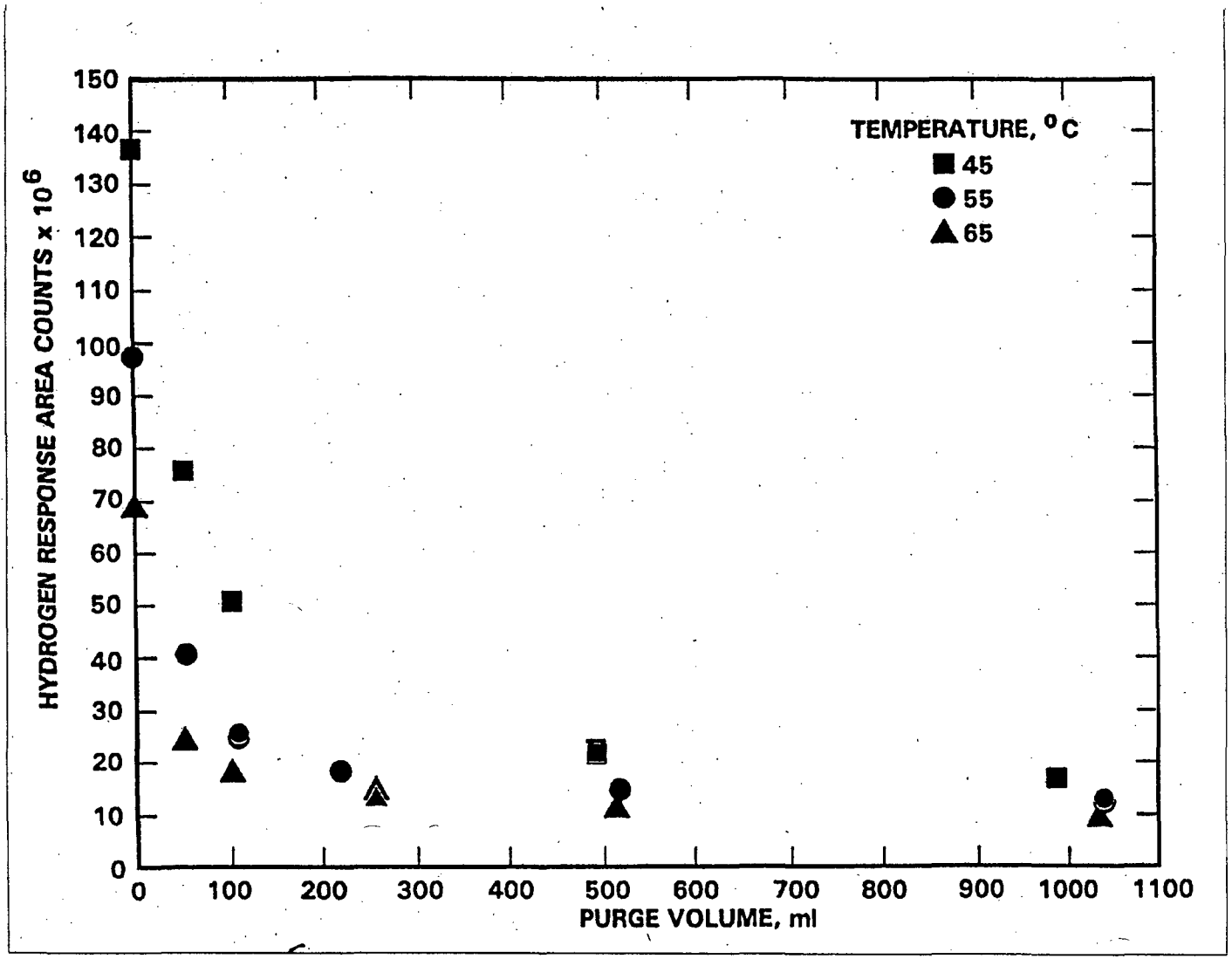



Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

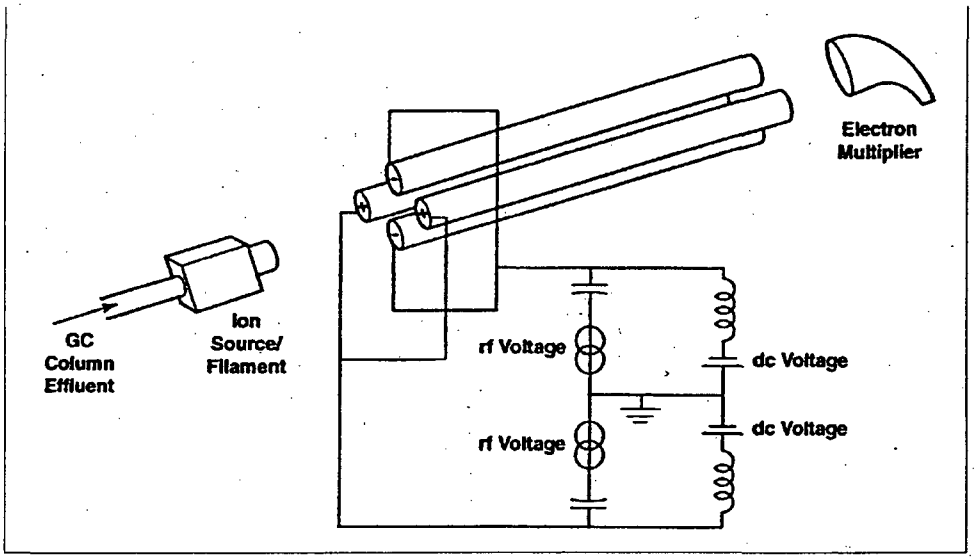



Figure 6. Simplified diagram of a quadrupole mass spectrometer.

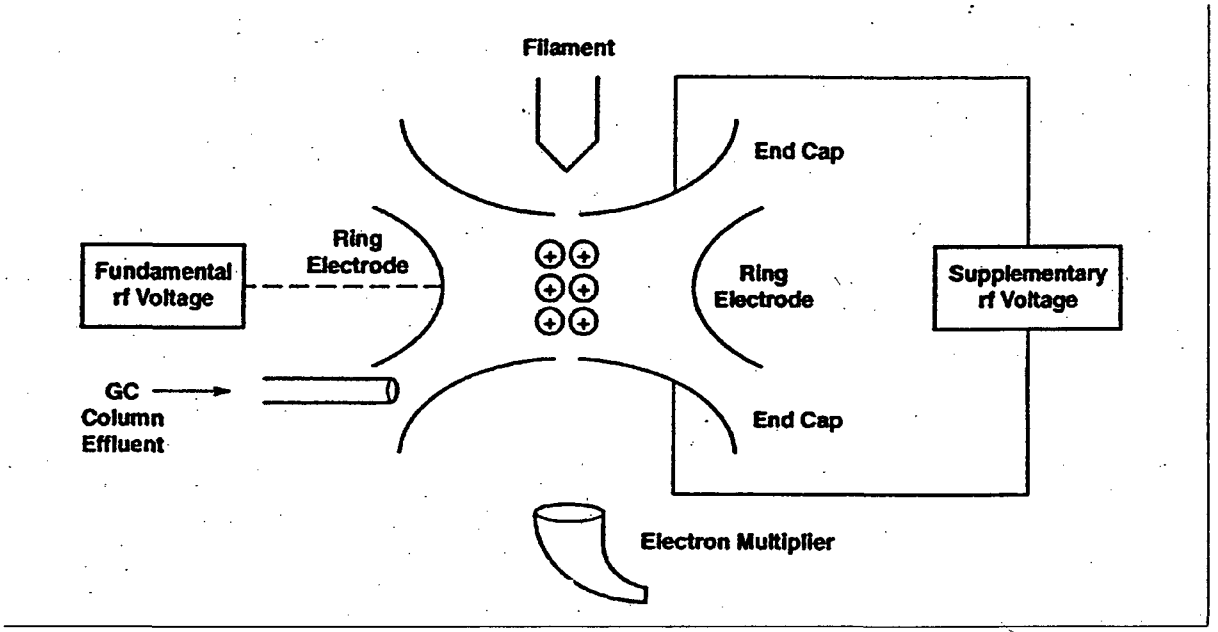



Figure 7. Simplified diagram of an ion trap mass spectrometer.

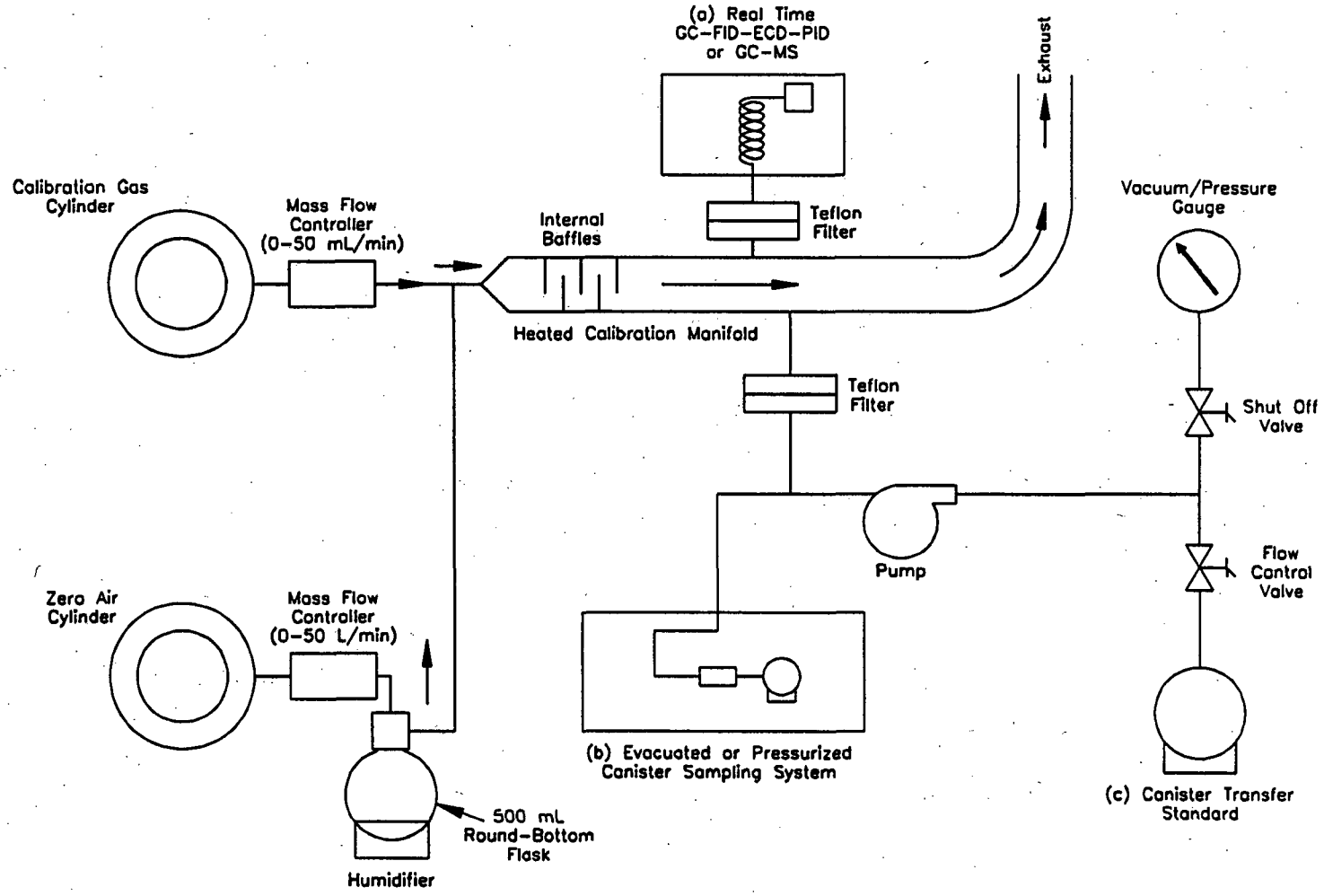



Figure 8. Schematic diagram of calibration system and manifold for
(a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

## COMPENDIUM METHOD TO-15
## CANISTER SAMPLING FIELD TEST DATA SHEET

**A.GENERAL INFORMATION**

SITE LOCATION: _____
SITE ADDRESS: _____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO.: _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK
CHECK DATE: _____

**B. SAMPLING INFORMATION**

| | TEMPERATURE | | | | PRESSURE | |
|---|---|---|---|---|---|---|
| | INTERIOR | AMBIENT | MAXIMUM | MINIMUM | CANISTER PRESSURE | |
| START | | | | | | |
| STOP | | | | | | |

| | SAMPLING TIMES | | FLOW RATES | | |
|---|---|---|---|---|---|
| | LOCAL TIME | ELAPSED TIME METER READING | MANIFOLD FLOW RATE | CANISTER FLOW RATE | FLOW CONTROLLER READOUT |
| START | | | | | |
| STOP | | | | | |

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

**C. LABORATORY INFORMATION**

DATA RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-FID-ECD DATE: _____
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS*: _____
_____
GC-FID-ECD: _____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

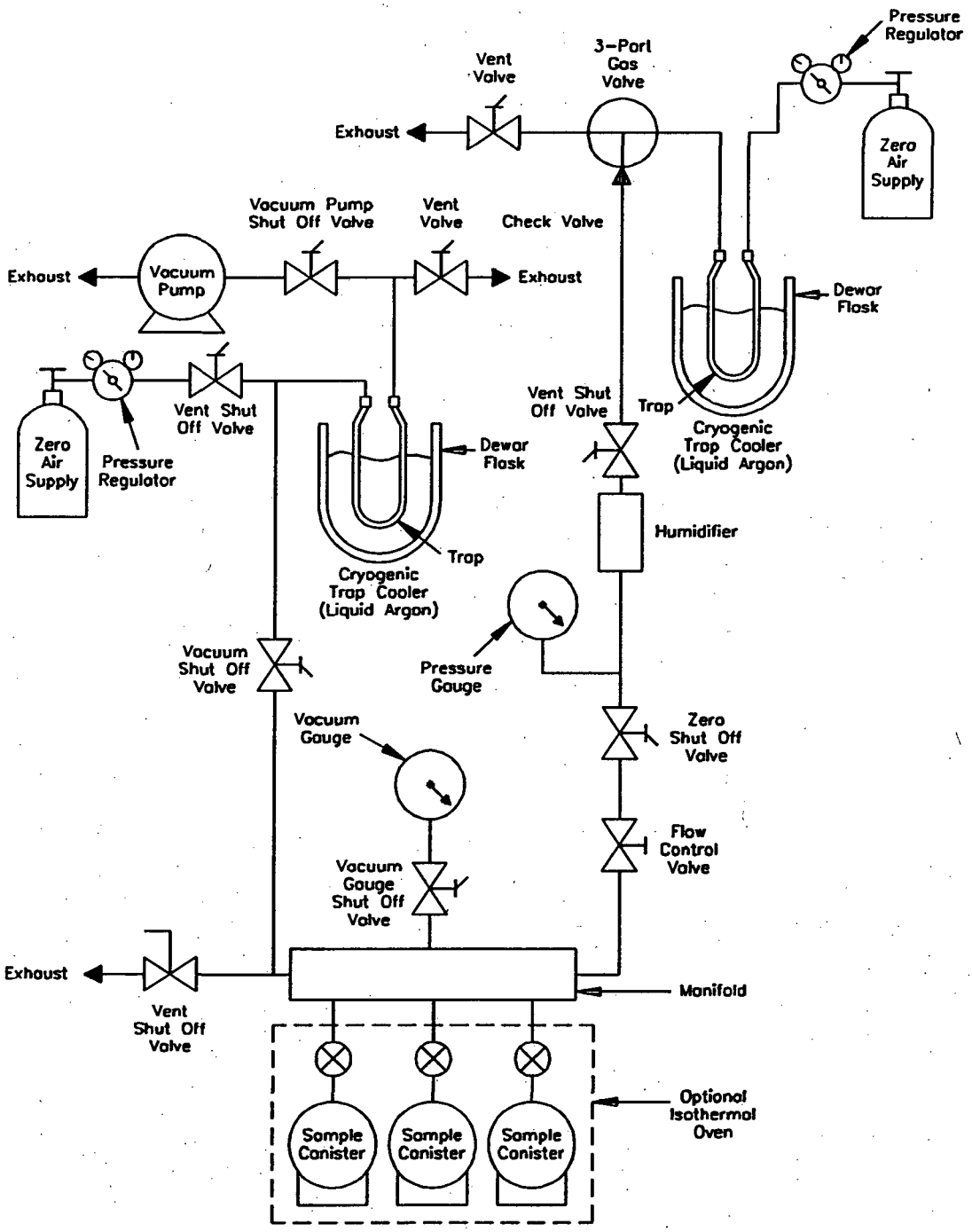



Figure 10. Canister cleaning system.

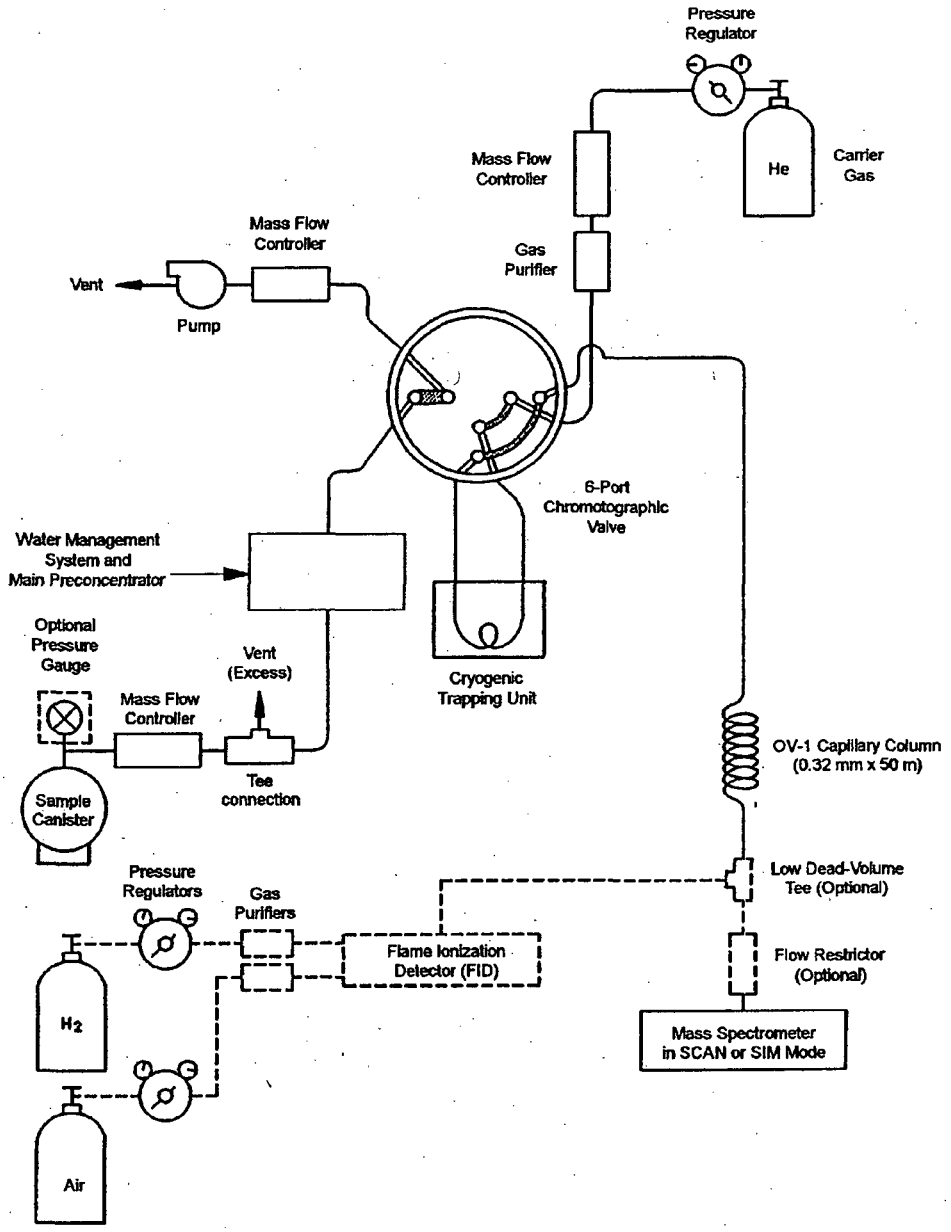
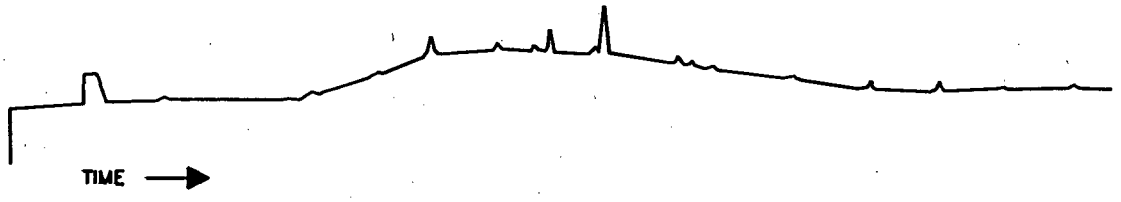
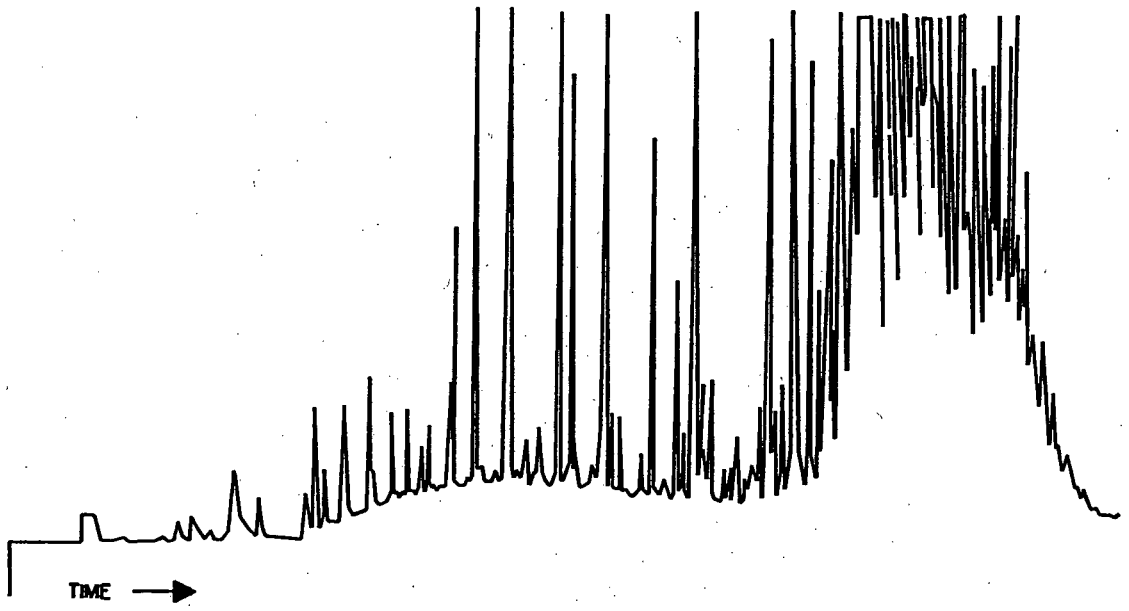



Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]




(a). Certified Sampler




(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

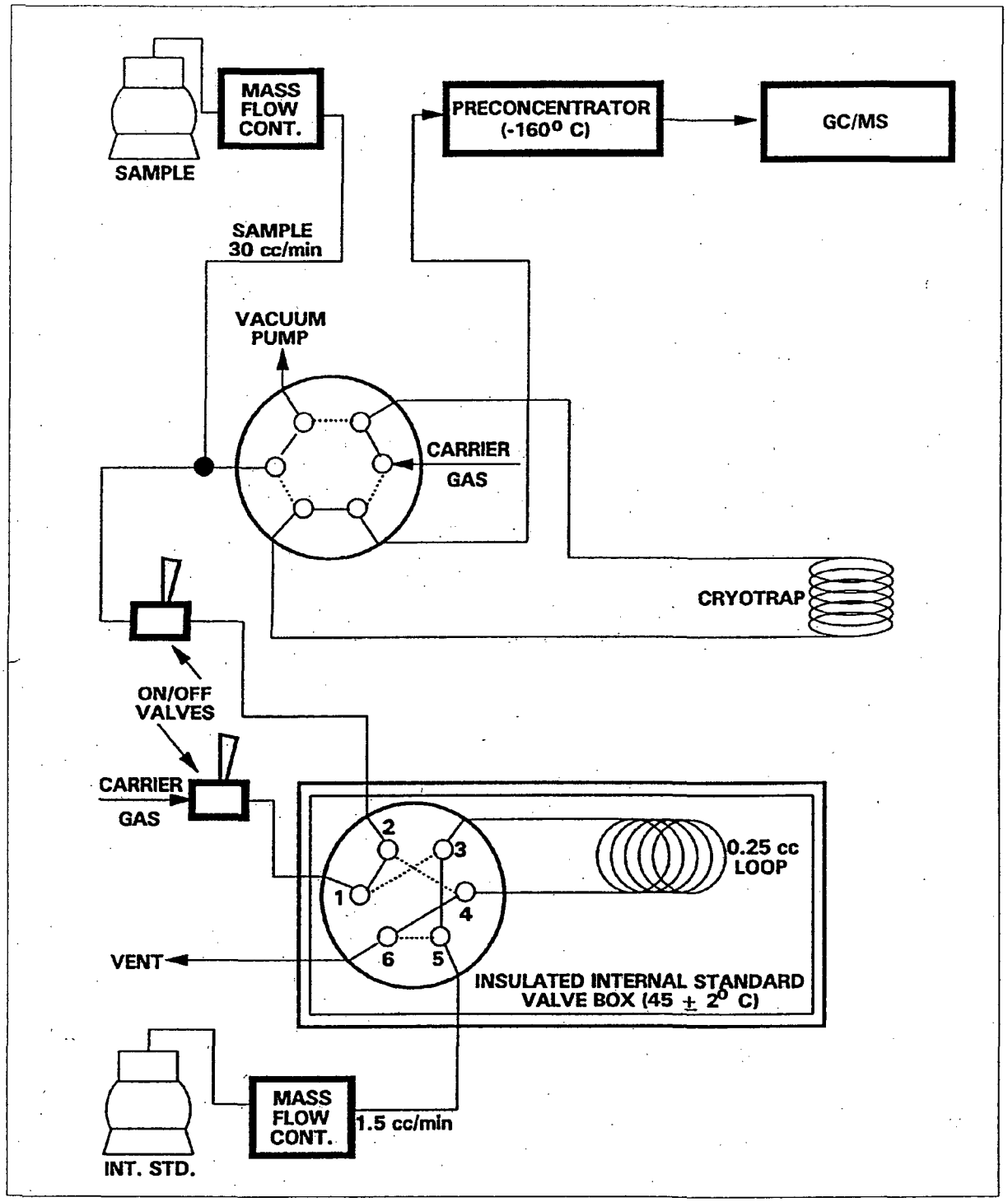



Figure 13. Diagram of design for internal standard addition.

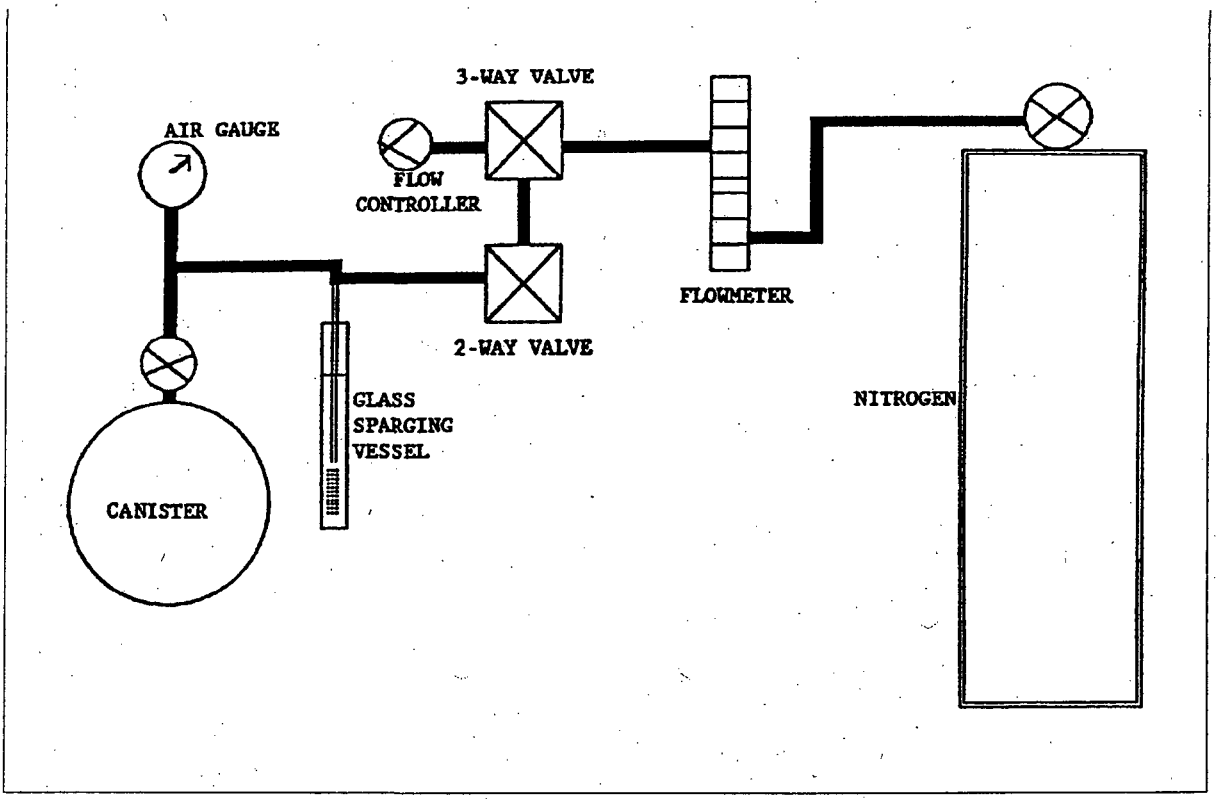



Figure 14. Water method of standard preparation in canisters.

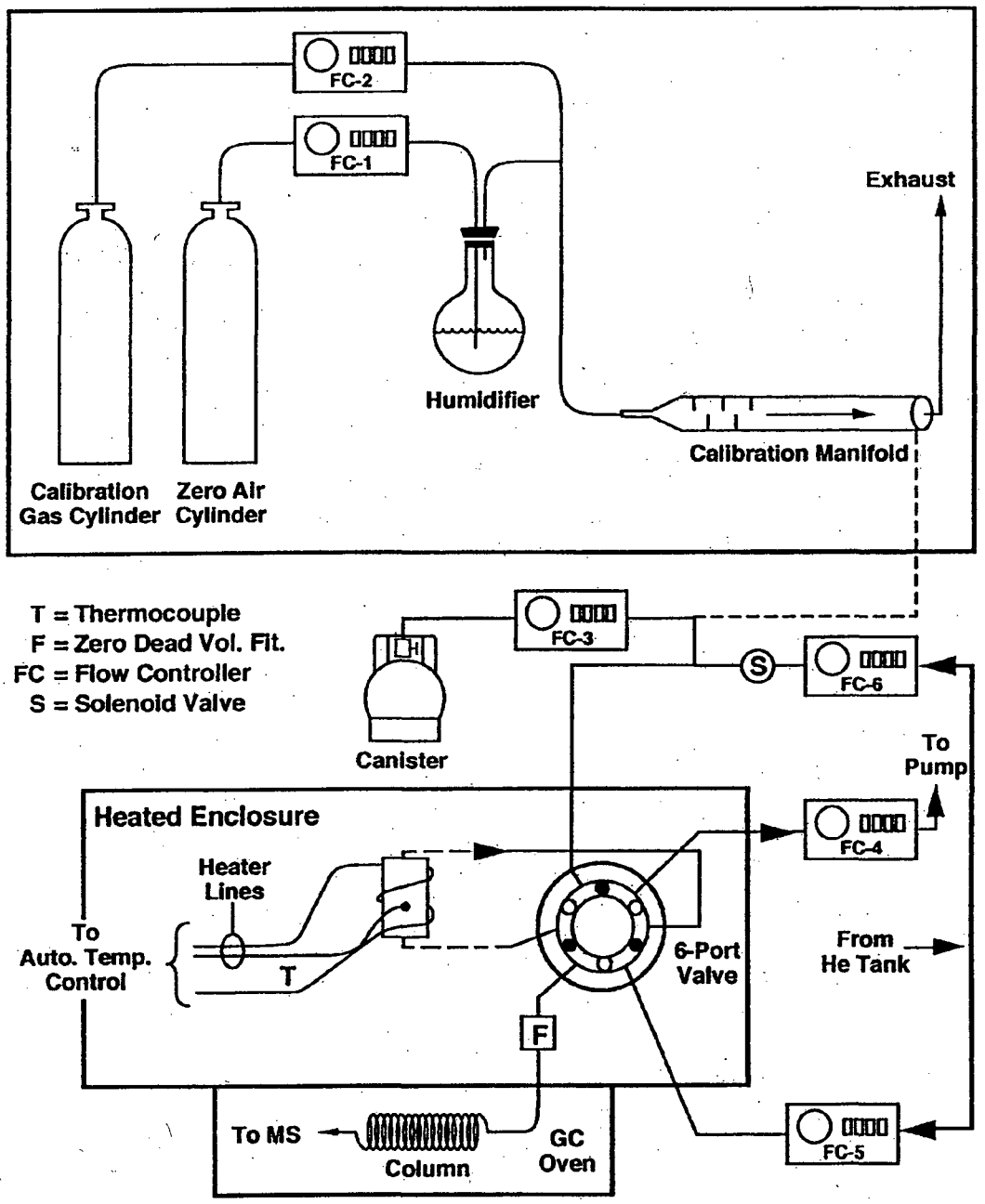



Figure 15. Diagram of the GC/MS analytical system.

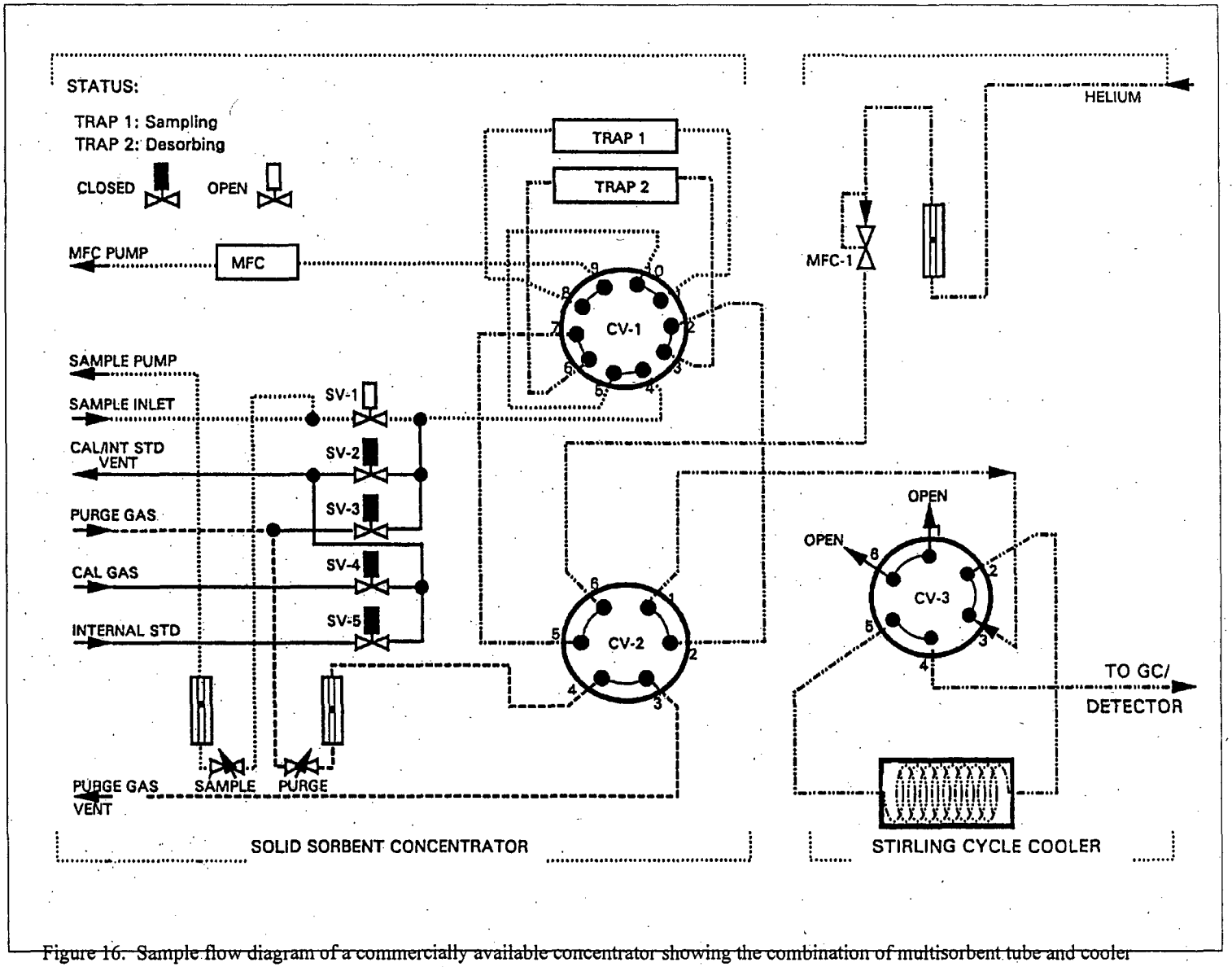



Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).

# SOP CHANGE -IN-PROGRESS ATTACHMENT (CIPA)

**SOP Title:** VOLATILE ORGANIC COMPOUNDS (VOCs) IN AIR BY (GC/MS)
**SOP No:** LM-AT-TO14/TO15
**Revision:** 4
**Date Effective:** 11/29/04

**CIPA Date Effective:** 11/18/05

**Change Approved By:**

**QA Manager:** Kirstin McCracken **Date:** November 18, 2005

Kirstin McCracken

**The following revisions or additions in BOLD TEXT were made to the referenced SOP. These changes were implemented on the CIPA Date Effective indicated above.**

## Page 16 of 19: Table 1

Table 1: Target Analyte List, RL, Quantitation Ions, Internal Standard and Calibration Goup Assignments

**Denotes TO-14 Target Analyte List*

*[1] TO-15 Target Analyte List*

| TO-14 | Analyte[1] | CAS No. | 6L RL (ppbv) | 1L RL (ppbv) | Quant Mass | Qualifier Mass | Qualifier Mass | ISTD Group | Cal Group |
|---|---|---|---|---|---|---|---|---|---|
| * | Dichlorodifluoromethane | 75-71-8 | 0.5 | 5 | 85 | 87 | | 1 | B |
| * | 1,2-Dichlorotetrafluoroethane | 76-14-2 | 0.2 | 2 | 85 | 135 | 87 | 1 | A |
| * | Chloromethane | 74-87-3 | 0.5 | 5 | 50 | 52 | | 1 | B |
| * | Vinyl Chloride | 75-01-4 | 0.2 | 2 | 62 | 64 | | 1 | A |
| | 1,3-Butadiene | 106-99-0 | ~~0.2~~ 0.5 | ~~2~~ 5 | 54 | 0 | | 1 | A |
| * | Bromomethane | 74-83-9 | 0.2 | 2 | 94 | 96 | | 1 | A |
| * | Chloroethane | 75-00-3 | 0.2 | 2 | 64 | 66 | | 1 | A |
| | Bromoethene | 593-60-2 | 0.2 | 2 | 106 | 108 | 81 | 1 | A |
| * | Trichlorofluoromethane | 75-69-4 | 0.2 | 2 | 101 | 103 | | 1 | A |
| * | Freon TF | 76-13-1 | 0.2 | 2 | 101 | 151 | 103 | 1 | A |
| * | 1,1-Dichloroethene | 75-35-4 | 0.2 | 2 | 96 | 61 | 63 | 1 | A |
| | Acetone | 67-64-1 | 5 | 50 | 43 | 58 | | 1 | C |
| | Isopropyl Alcohol | 67-63-0 | 5 | 50 | 45 | 43 | | 1 | C |
| | Carbon Disulfide | 75-15-0 | 0.5 | 5 | 76 | | | 1 | B |
| | 3-Chloropropene | 107-05-1 | ~~0.2~~ 0.5 | ~~2~~ 5 | 41 | 76 | | 1 | A |
| * | Methylene Chloride | 75-09-2 | 0.5 | 5 | 49 | 84 | 86 | 1 | B |
| | tert-Butyl Alcohol | 75-65-0 | 5 | 50 | 59 | 41 | 43 | 1 | C |
| | Methyl tert-Butyl Ether | 1634-04-4 | 0.5 | 5 | 73 | 43 | | 1 | B |
| | trans-1,2-Dichloroethene | 156-60-5 | 0.2 | 2 | 61 | 96 | | 1 | A |
| | n-Hexane | 110-54-3 | ~~0.2~~ 0.5 | ~~2~~ 5 | 57 | 86 | | 1 | A |
| * | 1,1-Dichloroethane | 75-34-3 | 0.2 | 2 | 63 | 65 | 83 | 1 | A |
| | 1,2-Dichloroethene (total) | 540-59-0 | 0.2 | 2 | 61 | 96 | | 1 | A |
| | Methyl Ethyl Ketone | 78-93-3 | 0.5 | 5 | 43 | 72 | | 1 | B |
| * | cis-1,2-Dichloroethene | 156-59-2 | 0.2 | 2 | 96 | 98 | | 1 | A |
| * | Chloroform | 67-66-3 | 0.2 | 2 | 83 | 85 | | 1 | A |
| | Tetrahydrofuran | 109-99-9 | 5 | 50 | 42 | 72 | | 2 | C |
| * | 1,1,1-Trichloroethane | 71-55-6 | 0.2 | 2 | 97 | 99 | 61 | 2 | A |
| | Cyclohexane | 110-82-7 | 0.2 | 2 | 84 | 56 | | 2 | A |
| * | Carbon Tetrachloride | 56-23-5 | 0.2 | 2 | 117 | 119 | | 2 | A |

Table 1 Continued

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2,2,4-Trimethylpentane | 540-84-1 | 0.2 | 2 | 57 | 41 | 43 | 2 | A |
| * | Benzene | 71-43-2 | 0.2 | 2 | 78 | 77 | | 2 | A |
| * | 1,2-Dichloroethane | 107-06-2 | 0.2 | 2 | 62 | 98 | | 2 | A |
| | n-Heptane | 142-82-5 | 0.2 | 2 | 43 | 71 | | 2 | A |
| * | Trichloroethene | 79-01-6 | 0.2 | 2 | 95 | 130 | 132 | 2 | A |
| | Methyl Methacrylate | 80-62-6 | 0.5 | 5 | 69 | 41 | 39 | 2 | B |
| * | 1,2-Dichloropropane | 78-87-5 | 0.2 | 2 | 63 | 41 | | 2 | A |
| | 1,4-Dioxane | 123-91-1 | 5 | 50 | 88 | 58 | | 2 | C |
| | Bromodichloromethane | 75-27-4 | 0.2 | 2 | 83 | 85 | | 2 | A |
| * | cis-1,3-Dichloropropene | 10061-01-5 | 0.2 | 2 | 75 | 110 | | 2 | A |
| | Methyl Isobutyl Ketone | 108-10-1 | 0.5 | 5 | 43 | 58 | | 2 | B |
| * | Toluene | 108-88-3 | 0.2 | 2 | 92 | 91 | | 3 | A |
| * | trans-1,3-Dichloropropene | 10061-02-6 | 0.2 | 2 | 75 | 110 | | 2 | A |
| * | 1,1,2-Trichloroethane | 79-00-5 | 0.2 | 2 | 83 | 97 | 85 | 3 | A |
| * | Tetrachloroethene | 127-18-4 | 0.2 | 2 | 166 | 168 | 129 | 3 | A |
| | Methyl Butyl Ketone | 591-78-6 | 0.5 | 5 | 43 | 58 | | 3 | B |
| | Dibromochloromethane | 124-48-1 | 0.2 | 2 | 129 | 127 | | 3 | A |
| * | 1,2-Dibromoethane | 106-93-4 | 0.2 | 2 | 107 | 109 | | 3 | A |
| * | Chlorobenzene | 108-90-7 | 0.2 | 2 | 112 | 77 | 114 | 3 | A |
| * | Ethylbenzene | 100-41-4 | 0.2 | 2 | 91 | 106 | | 3 | A |
| * | Xylene (m,p) | 1330-20-7 | ~~0.2~~ 0.5 | ~~2~~ 5 | 106 | 91 | | 3 | A |
| * | Xylene (o) | 95-47-6 | 0.2 | 2 | 106 | 91 | | 3 | A |
| * | Styrene | 100-42-5 | 0.2 | 2 | 104 | 78 | | 3 | A |
| | Xylene (total) | 1330-20-7 | 0.2 | 2 | 106 | 91 | | 3 | A |
| | Bromoform | 75-25-2 | 0.2 | 2 | 173 | 175 | 171 | 3 | E |
| * | 1,1,2,2-Tetrachloroethane | 79-34-5 | 0.2 | 2 | 83 | 131 | 85 | 3 | A |
| | 4-Ethyltoluene | 622-96-8 | 0.2 | 2 | 105 | 120 | | 3 | A |
| * | 1,3,5-Trimethylbenzene | 108-67-8 | 0.2 | 2 | 105 | 120 | | 3 | A |
| | 2-Chlorotoluene | 95-49-8 | 0.2 | 2 | 91 | 63 | | 3 | A |
| * | 1,2,4-Trimethylbenzene | 95-63-6 | 0.2 | 2 | 105 | 120 | | 3 | A |
| * | 1,3-Dichlorobenzene | 541-73-1 | 0.2 | 2 | 146 | 111 | 148 | 3 | A |
| * | 1,4-Dichlorobenzene | 106-46-7 | 0.2 | 2 | 146 | 111 | 148 | 3 | A |
| * | 1,2-Dichlorobenzene | 95-50-1 | 0.2 | 2 | 146 | 111 | 148 | 3 | A |
| * | 1,2,4-Trichlorobenzene | 120-82-1 | 0.5 | 5 | 180 | 182 | | 3 | B |
| * | Hexachlorobutadiene | 87-68-3 | 0.2 | 2 | 225 | 223 | | 3 | A |
| | Naphthalene | 91-20-3 | 0.5 | 5 | 128 | | | 3 | D |
| | **Internal Standards** | | | | | | | | |
| * | Bromochloromethane | 74-97-5 | NA | NA | 128 | 49 | 130 | 1 | NA |
| * | 1,4-Difluorobenzene | 540-36-3 | NA | NA | 114 | | | 2 | NA |
| * | Chlorobenzene-d5 | 3114-55-4 | NA | NA | 117 | | | 3 | NA |

SEVERN TRENT STL



# STANDARD OPERTING PROCEDURE
## VOLATILE ORGANIC COMPOUNDS (VOCs) IN AIR BY (GC/MS)
### EPA Compendium Method TO-14 / EPA Compendium Method TO-15

Applicable Matrix: Air

Standard Compound List and Reporting Limits: See Table 1

**Approvals and Signatures**

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 11/15/04

QA Manager: Kirstin L. McCracken Date: 11-15-04

Department Manager: Bryce E. Stearns Date: 11/15/04

## 1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for analysis of polar and non-polar volatile organic compounds (VOCs) in ambient air. The procedure is applicable to those VOCs that have been evaluated by the laboratory for their consistent performance in meeting the control criteria put forth in Compendium Method TO-15. While the compendium method is specifically written for the analysis of samples collected in leak-free passivated stainless steel canisters, it may be applied to the analysis of samples that have employed the use of other collection devices such as Tedlar bags and solid absorbents.

1.2 The target compound list(s) are given in Table 1 along with the reporting limit (RL).

## 2.0 SUMMARY OF METHOD

2.1 A sample submitted for analysis is directed from the sample container through a series of solid sorbent bed traps, which also reduces the water content of the sample. The sample is thermally desorbed and the VOCs are carried onto a gas chromatographic column coupled to a mass spectrometer. Compounds are identified by comparison of the mass spectra for individual peaks in the total ion chromatogram to the fragmentation patterns of ions corresponding to VOCs including the intensity of primary and secondary ions as well as the patterns of stored spectra taken under similar conditions. The concentration of the target compound is calculated by internal standard technique using the average response factor of that compound as determined by the initial calibration.

2.2 This procedure is based on Compendium Methods TO-14 and TO-15, Determination of Volatile Organic Compounds (VOCs) In Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS). USEPA Office of Research and Development, Cincinnati OH, January 1999.

## 3.0 DEFINITIONS

**Absolute Pressure**-pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg, or psia.

**Cryogen**-a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid nitrogen (bp –195.8°C) or liquid argon (bp –185.7°C).

**Internal Standards (IS)**-Non-target analyte compounds that are similar to the target analytes but are not expected to be found in environmental media (generally, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to analysis. IS responses are used as the basis for quantitation of target analytes.

**Stock solutions**-A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

**Calibration Standard (CAL)**-A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

**Continuing Calibration Verification (CCV)**-An analytical standard solution containing all target analytes and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

**Method Blank**-A canister of ambient air or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The ABLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

**Laboratory Control Sample (LCS)**-The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

**Initial Calibration Verification (ICV)**-An analytical standard solution containing all target analytes and internal standard compounds that are prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

## 4.0 INTERFERENCES

4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus does not contaminate samples.

## 5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.1 Specific Safety Concerns or Requirements

The analytical system contains zones with elevated or depressed temperatures that are capable of causing injury upon direct contact. The analyst needs to be aware of the

locations of those zones, and allow them to return to room temperature prior to maintenance activities or take measures to avoid contact with hot and/or cold surfaces.

There are areas of high voltage in the analytical system. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

Liquid nitrogen (LN2) is used for cryogenic purposes. In addition to avoiding contact with LN2 cooled surfaces, analysts must be aware of the potential for oxygen depletion in a confined space in the event of an unexpected large release of the product. Users should evacuate a confined space in which large amounts of LN2 have been released.

Sample canisters are occasionally pressurized for cleaning or sample dilution purposes. Lab systems are designed to ensure that the cans are not pressurized above 32 psi. Eye protection must be worn when cans are pressurized in the event of a canister failure.

5.2 Primary Materials Used

The materials used in this method are generally commercially prepared gas phase standards. On rare occasions, gas phase standards may be formulated from neat materials. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Canisters

SUMMA® Leak-Free Passivated Stainless Steel Canisters, 1 and 6 Liter, Restek Catalog #555656 or equivalent.

Vacuum Pressure Gauges / Flow Controllers, Restek Catalog #24239 or equivalent.

*Note: The catalog numbers listed in this SOP are subject to change.*

6.2 Analytical System

VOC Autosampler, Entech 7016CA or equivalent.

Cryogenic Concentrator equipped with an electronic mass flow controller that maintains a constant flow for carrier gas and sample over a range of 0-200 cc/min. Entech 7100A or equivalent.

Multisorbent Bed Cryotrap capable of effectively removing water and $CO_2$ while trapping polar and non-polar compounds.

Gas Chromatograph: Agilent 6890 or equivalent

Mass Spectrometer: Agilent 5973 or 5972 MSD or equivalent

Primary Column: Fused silica capillary column, Restek RTX-624 60m x 0.32 mm x 1.8 µm or equivalent

Vacuum Pumps

Syringes-1.0 mL - 1.0 L gas tight syringes with Luer-Lok tip

Data System: PC software for Entech instrumentation. Hewlett-Packard ChemStation data acquisition software and Hewlett-Packard ChemServer, Target 3.5 data processing software

Canister Cleaning System: Entech auto-canister cleaning system, Model 3000 or 3100 or equivalent.

Vacuum Pump: Capable of evacuating sample canisters to a vacuum of -29.9" Hg.

Manifold: Equipped with stainless steel and Teflon transfer lines and connections for cleaning up to eight canisters simultaneously.

Vacuum Gauge: Capable of measuring vacuum in the manifold to an absolute pressure of 0.05-mm Hg or less.

Heating Manifolds: Individually thermal-stated heating manifolds used to heat canisters during the cleaning cycle.

Tedlar Bag

## 7.0 REAGENTS AND STANDARDS

### 7.1 Standards

Unless otherwise noted gaseous standards are stored at room temperature and assigned an expiration date of three months.

4-Bromofluorobenzene (BFB) Working Standard (100 ppbv): Spectra Gases or equivalent.

Gaseous Stock Standard 1: A commercially purchased gaseous stock standard that includes all target compounds except for naphthalene at a concentration of 1.0 ppmv. Spectra Gases or equivalent.

Gaseous Stock Standard 2: A commercially purchased standard that includes naphthalene at a concentration of 1.0 ppmv and bromoform at a concentration of 3.0 ppmv. Spectra Gases or equivalent.

Intermediate Standards: Prepare intermediate standards by adding a known amount of the stock standard(s) into a SUMMA canister and pressurizing the canister with humidified (relative humidity >20 percent) zero air to achieve the concentrations given in the following table:

| Intermediate Standard | Component(s) | Volume Added (mL) | Final Concentration (ppbv) |
|---|---|---|---|
| 1 | Stock Standard 1 | 495 | 40 |
| 2 | Stock Standard 1 | 125 | 10 |
| 3 | Intermediate Standard 1 | 495 | 0.5 |
| 4 | Stock Standard 1, Stock Standard2 | 495 | 40 |
| 5 | Stock Standard 1, Stock Standard 2 | 125 | 10 |
| 6 | Intermediate Standard 4 | 495 | 0.5 |

Internal standards: (Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5) are purchased from Spectra Gases at a concentration of 1 ppmv. 20 mL of each internal standard is introduced directly to the concentrator to volumes sufficient to achieve a final concentration of 10 ppbv in sample.

Laboratory Control Sample: A multi-component stock standard purchased from commercial vendor, Spectra Gases. Prepare the working LCS standard by adding 125 mL to a canister and then pressurizing the canister with humidified zero air to achieve the target concentration, which is at or near the midpoint of the calibration curve.

## 8.0 SAMPLE COLLECTION, PRESERVATION & STORAGE

8.1 The laboratory recommends that samples be collected in passivated stainless steel canisters that have been cleaned and tested prior to sampling. The ability to collect a representative sample, particularly for the higher boiling compounds, is highly dependent on such factors as the length of the sampling train and the materials of construction, the temperature and relative humidity at which sampling occurs, and the sampling flow rate. Because the laboratory does not perform sample collection, specific sampling procedures are not provided in this SOP. Guidance for sample collection may be found in the published reference methods for Compendium Methods TO-14 and TO-15. After collection samples may be stored at ambient temperature until analysis.

8.2 The analytical holding time for samples collected in passivated stainless steel canisters is 30 days from the date of collection.

8.3 Unless otherwise specified by client or regulatory program, after analysis sample canisters are cleaned in accordance with the procedure given in Section 11.1.

## 9.0 QUALITY CONTROL

This section provides a brief description of the QC check samples analyzed with this method. The minimum frequency requirements, acceptance criteria and recommended corrective action for all QC samples are summarized in Section 17.0, Table 3.

The following QC samples are analyzed with each analytical batch: a Method Blank (MB), Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD). Sample duplicates are performed per client request.

Internal standards are added to all calibration standards, samples, and blanks to verify that the analytical system is in control.

## *10.0 CALIBRATION AND STANDARDIZATION*

### 10.1 Instrument Performance Check (BFB)

Every 24 hours, prior to the acquisition of a calibration curve or the analysis of samples, analyze a BFB standard following the procedure given in section 11.2. The results of the BFB analysis must meet the mass spectral ion abundance criteria given in Table 2. If the acceptance criteria are not met, perform instrument maintenance and reanalyze the tune standard.

### 10.2 Initial Calibration

After the criteria for the tune standard are met, calibrate the instrument with a minimum of five calibration standards for each target analyte at concentrations that span the working range of the system. The recommended concentrations for the calibration standards are 0.2, 0.5, 5, 10, 15, 20, and 40 ppbv. The 15 ppbv calibration point is specific to acetone, isopropyl alcohol, tertiarybutyl alcohol, tetrahydrofuran, and 1,4-dioxane. These compounds are not included in either the 0.2 ppbv or the 0.5 ppbv calibration points. Additionally, naphthalene is not included in the 0.2ppbv standard. The standard for naphthalene is formulated with one and possibly more of the other target analytes. For this reason there is a separate 0.5 ppbv acquisition specific to naphthalene. This provides for the low calibration point for napthalene without affecting the concentration of each of the target analytes at the 0.5 ppbv concentration level. The remaining calibration points (5, 10, 20, and 40 ppbv) are acquired with the inclusion of the naphthalene standard, and the concentration of co-formulated compounds needs to be included in developing the response factors for these compounds. For ease of reference, each calibration standard is assigned one of the following calibration group identifiers: A, B, C, D, E, which can be cross-referenced to the target analytes listed in Table 1 in order to determine which calibration level is used.

The working calibration standards are introduced to the GC/MS by injecting the appropriate volume(s) of the intermediate standards directly into the sample concentrator following the procedure that begins in Section 11.3. The injection volume and final concentration for each calibration level is provided in the following table but is

subject to change if the composition or concentration for any parent component standard should change or if the working range of the calibration should be adjusted.

| Calibration Level | Intermediate Standard | Calibration Group Identification | Volume Injected (mL) | Final Concentration (ppbv) |
|---|---|---|---|---|
| 1 | Standard 3 | A, E | 80 | 0.2 |
| 2 | Standard 3 | E | 200 | 0.5 |
| 3 | Standard 6 | A, B, D, E | 200 | 0.5 |
| 4 | Standard 5 | A, B, C, D, E | 100 | 5.0 |
| 5 | Standard 5 | A, B, C, D, E | 200 | 10.0 |
| 6 | Standard 4 | C | 75 | 15.0 |
| 7 | Standard 4 | A, B, C, D | 100 | 20.0 |
| 8 | Standard 4 | A, B, C, D | 200 | 40.0 |

The data system calculates a relative response factor (RRF) for each analyte and/or isomer pair for each calibration standard using the appropriate internal standard. (See Table 1 for internal standard assignments). The data system then calculates a mean *relative response factor, percent relative standard deviation, relative retention time* (RRT) and the mean RRT. The %RSD for each compound must be < 30%, **with at most two exceptions up to a limit of 40%*.** The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound. The retention time shift for each of the internal standards at each calibration level must be within 20 seconds of the mean retention time over the initial calibration range for each internal standard. If these criteria are not met, inspect the system for problems and recalibrate.

**This exception may not be applicable to project specific compounds.*

Perform initial calibration prior to any sample analysis (initial method set-up), whenever a new column is installed, when significant instrument maintenance has been performed, and when the CCV standard does not meet acceptance criteria.

10.3 Initial Calibration Verification

Immediately following an acceptable initial calibration, verify the accuracy of the calibration with a second source standard (ICV). For this procedure the laboratory control sample serves as the ICV. The procedures for the preparation and analysis of the ICV/LCS are provided in Section 11.3. The percent recovery of the ICV/LCS should be within 70-130%. If criteria are not met, correct the problem and reanalyze the ICV/LCS. If the reanalysis fails, remake the calibration standards and recalibrate.

10.4 Daily Calibration Check

Analyze a continuing calibration verification (CCV) standard each day prior to sample analysis, to ensure the instrument is reliable and has not changed significantly from the current initial calibration curve. The CCV should include all target analytes and the

concentration of the CCV standard should be at or below the middle of the calibration range and varied within the calibration range. Analyze the CCV following the procedure that begins in Section 11.3.

The data system calculates a response factor for each analyte along with the percent difference of the RRF to the mean RRF in the most recent initial calibration. The %D for each target compound must be within ±30%. If this criterion is not met, correct the problem prior to further analysis.

## 11.0 PROCEDURE

### 11.1 Canister Cleaning & Certification Procedure

Each canister must be certified clean prior to its initial use for sample collection. Thereafter one canister from each cleaning batch is analyzed to verify that the cleaning procedure was effective for all canisters in the cleaning batch. The canister chosen for analysis should always be the canister that had the highest target/TIC concentration from the previous sample analysis. If no targets are detected in the "certification" canister analyzed, then it is presumed the cleaning procedure was effective and all other canisters cleaned within the same cleaning batch are certified as clean.

Procedure:

Connect the canister(s) to the manifold. Open the vent shut-off valve and the canister valve(s) to release any remaining pressure in the canister(s). Attach the heating band(s) to the canister(s) and turn on the current, allowing the bands to heat to 100 °C. Establish the number of cycles (≥3 for 6 L canisters and ≥6 for 1 L canisters) on the cleaning system and depress the "Auto" button.

After the evacuation/pressurization cycles are complete, pressurize the certification canister to 10 psig with humidified zero air and analyze this canister using the procedure that begins in Section 11.3. No analytes should be detected in this canister above the RL. If this criterion is not met, repeat the cleaning procedure.

After an acceptable certifying analysis, re-attach the canister to the cleaning manifold and evacuate the canister to <-29.5" Hg. Close the canister valve and remove the canister from the cleaning apparatus. Cap the canister with a swagelock fitting and initial and date the canister identification tag. Complete the Canister Certification Report, attach supporting data to the report and retain on file.

Prior to shipment of canisters to the client, perform a leak test on each canister by evacuating the canister to approximately -29.5"Hg. Measure the initial vacuum, close the valve then recheck the vacuum after at least 24 hours has elapsed. The vacuum should not vary more than 0.5"Hg over the time period for the leak test to be considered acceptable. If there is a loss of more than 0.5" Hg, the canister is to be removed from service.

11.2 Instrument Operating Conditions

Optimize the GC and MS conditions for compound separation and sensitivity. The recommended operating conditions are as follows:

| | |
|---|---|
| Carrier Gas: | Helium, Ultra High Purity |
| Cyrogenic Focusing Gas: | Liquid Nitrogen |
| Flow Rate: | ~1.5mL/min |
| Temperature Program: | Initial Temperature: 40°C |
| | Initial Hold Time: 4 minutes |
| | Ramp1 Rate: 20°C/min. to 200°C. |
| | Ramp 2 Rate: 40°C/min. to 220°C |
| | Final Temperature: 220°C |
| | Final Hold Time: 6.5 minutes |
| Electron Energy: | 70 electron volts |
| Mass Range: | 35-265amu |
| Scan Time: | ≥ 1 scan per second |

These operating conditions may be changed but once the operating conditions are established the same conditions must be used for both calibration and analysis of field samples.

11.2 Sample Preparation

Inspect the condition of each sample container on receipt and notify the laboratory Project Manager of any signs of damage. Check the pressure of each sample canister by attaching a pressure gauge to the canister inlet and briefly opening the canister valve to obtain the pressure reading. Notify the laboratory Project Manager if the residual vacuum is greater than -10.0" Hg (- 5.0" Hg for 1 L canisters), or when there is no residual vacuum. Adjust the pressure of canisters received at a vacuum of greater than –10.0" Hg with zero grade air to ensure that sample volume can be withdrawn for analysis. Record the final pressure and calculate and record the dilution factor, using the "Canister Dilution Worksheet".

11.3 Sample Analysis

Set up the analytical run in the following sequence:

BFB Tune
Initial Multi-Point Calibration or Daily Calibration Check
ICV/LCS
LCSD
Method Blank
Field Samples

Set the MS system so that it scans the atomic mass range from 35 to 265 amu with acquisition of at least 1 scan per second. Introduce the BFB standard directly to the

instrument concentrator, and thermally desorb into the GC/MS system. Acquire the data for the BFB tune and evaluate the results against the criteria given in Table 2. If the acceptance criteria are not met, perform corrective action prior to further analysis.

Introduce each calibration standard directly to the instrument concentrator, with the addition of internal standards equivalent to 10 ppbv. Analyze the standards in a sequence from lowest to highest concentration. Thermally desorb into the GC/MS system, and acquire the data. Evaluate the results against the criteria given in Table 3, Section 17.0. If the acceptance criteria are not met perform corrective action prior to further analysis.

Analyze the CCV, alternating the concentration of the CCV between 10 ppbv and 20 ppbv. Acquire the data and evaluate the results against the criteria given in Table 3, Section 17.0. If the acceptance criteria are not met perform corrective action prior to further analysis.

If time remains in the 24-hour period immediately following an initial calibration, samples may be analyzed without analysis of the daily calibration standard. Otherwise, an instrument performance check (BFB) and daily calibration check must be analyzed prior to samples.

Prepare the laboratory control sample(s) (ICV/LCS, LCSD) according to the procedure given in Section 7.2. Attach the canister to an autosampler inlet and introduce 200 mL of volume to the instrument concentrator for a 6 L canister (20 mL for a 1 L canister), with the addition of internal standards equivalent to 10 ppbv. Thermally desorb into the GC/MS system.

Analyze the method blank by introducing 200 mL of humidified zero air, with the addition of internal standards equivalent to 10 ppbv, to the concentrator. Thermally desorb into the GC/MS system.

Analyze field samples in a consistent manner by introducing 200 mL of volume (20 mL of volume for 1 L canisters) to the instrument concentrator. Thermally desorb the sample into the GC/MS system.

Acquire the data and evaluate the results (See Section 13.0). The data system identifies target analytes by comparison of the mass spectrum (after background subtraction) to a reference spectrum in the user created database and calculates the concentration of target analytes in ppbv using the equation given in Section 12.0. If the on-column concentration of any sample exceeds the range of calibration (40 ppbv), reanalyze an aliquot of the original sample at an appropriate dilution.

When the aliquot to be analyzed is less than 20 milliliters, prepare the dilution by pressurizing the canister, and document the dilution using the canister dilution worksheet. The maximum pressurization set by the laboratory is 30 psig. This, with the smaller sample aliquot, provides for dilutions of up to 30-fold on the base method, or the ability to provide for constituent concentrations of nominally 1000 ppbv. Samples

requiring a greater dilution are considered to be outside the scope of the TO-15 method. If these samples are to be analyzed with the quantification of responses within the calibrated range, perform a secondary dilution into a Tedlar bag, using a gas-tight syringe and humidified air. In performing this type of dilution, prepare and analyze a method blank and a laboratory control sample using the same technique and materials that are used in the preparation of the sample(s).

Samples containing carbon dioxide and/or methane approximating 1 percent by volume may significantly affect analytical performance when a 200 mL sample volume is analyzed. Such samples are to be diluted for analysis, the reason for the dilution noted on the analytical run-log, and the Project Manager notified of the situation.

The application of the method to the analysis of samples collected in Tedlar bags is outside the scope of the TO-15 method, however certain project work may employ the use of this collection device. If samples are to be analyzed from Tedlar bags, prepare and analyze a method blank and a laboratory control sample using the same technique and materials that are used in the preparation of the sample(s).

11.4 Data Reporting

Report the results with target concentrations less than the RL as RL "U". Report the results above the RL as the target concentration. Adjust the reporting limit (RL) for sample dilution/concentration and apply data qualifiers as appropriate. The laboratory's RL for each target analyte is provided in Table 1.

Report the result of samples collected in Tedlar bags, or diluted in Tedlar bags, using the RL from Table 1 adjusted for sample dilution and associate the samples results with the Tedlar bag blank and Tedlar bag LCS.

Some projects may require MDL↔RL reporting, when this is the case, report the values between the MDL and the RL as estimated indicating that in this region (MDL↔RL) the analyte can be qualitatively detected by not accurately quantified. Flag all results reported between the MDL and RL with a "J" data qualifier.

Some project may require RLs that are less than the laboratory's routine RL. Sample results may be reported to the project RL if the project RL is greater than the quantitation limit (QL). In this context, the QL is defined as the concentration of the low calibration standard. If the project RL is less than the QL, all values less than the QL must be reported as estimated and qualified with a "J".

Further guidance on the application and use of method detection limits (MDLs), reporting limits (RLs) and quantitation limits (QL) for the reporting analytical data is provided in laboratory SOP LP-LB-009 *Determination of Method Detection Limits.*

## 12.0 CALCULATIONS

12.1 Equation 1: Dilution Factor

$$DF = \frac{V_2}{V_1} x \frac{V_4}{V_3}$$

Where:
$V_1$ = Canister gas volume before dilution
$V_2$ = Canister gas volume after dilution
$V_3$ = gas volume analyzed
$V_4$ = gas volume basis of the analysis (200mL)
$V_5$ = gas volume used in secondary dilution
$V_6$ = final volume of secondary dilution

12.2 Equation 2: Relative Response Factor (RRF)

$$RRF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

Where:
$A_x$ = area of the quantitation ion of the analyte
$A_{is}$ = area of the quantitation ion of the internal standard
$Q_x$ = quantity of analyte purged in nanograms or concentration units
$Q_{is}$ = quantity of internal standard purged in ng or concentration units

12.3 Equation 3: Percent Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{Mean} x100$$

Where:
SD = standard deviation individual response factors
Mean = average of initial calibration response factors

12.4 Equation 4: Sample Concentration

$$C_x = \frac{(A_x)(C_{IS})}{(A_{IS})(RRF)}(DF)$$

Where:
$C_x$ = Compound concentration, (ppbv)
$C_{IS}$ = Concentration of associated internal standard (ppbv).
$A_{IS}$ = Area of quantitation ion for associated internal standard
$A_x$ = Area of quantitation ion for compound
DF = Dilution Factor

Mean RRF = Average Relative Response Factor from initial calibration.

12.8 Equation 8: Percent Recovery (%R)

$$\%R = \frac{C_s - C_u}{C_n}(100)$$

Where:
$C_s$ = Concentration of the spiked sample
$C_u$ = Concentration of the unspiked sample
$C_n$ = Nominal concentration of spike added

12.9 Equation 9: Precision (%RPD)

$$RPD = \frac{(C_1 - C_2)}{\left(\frac{C_1 + C_2}{2}\right)}(100)$$

Where:
$C_1$ = Measured concentration of the first sample
$C_2$ = Measured concentration of the second sample

## 13.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTION

13.1. Data Review and Corrective Action

Review the samples, standards and QC samples against the acceptance criteria given in Table 3*. If the results do not fall within the established limits perform the recommended corrective action. If corrective action is not taken or is unsuccessful, document the situation with a nonconformance report and qualify the data using an appropriate data qualifier (See Appendix C for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review*.

## 14.0 METHOD PERFORMANCE

14.1. A demonstration of capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC procedures are further described in laboratory SOP LP-QA-011, *Employee Training*.

14.2. A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period and when there is a significant change to the analytical system. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009 Method Detection Limits. The laboratory considers an MDL

study based on the performance defined by the analysis from a 6 L canister as having a direct application to the analysis from a 1 L canister, with a scalar relationship of the established MDL to the volume analyzed. The application of the method to the analysis of samples collected in Tedlar bags is outside the scope of the TO-15 method, and MDL studies specific to this collection device are not routinely performed by the laboratory.

## 15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies given in Section 13 of the Corporate Safety Manual for Waste Management and Pollution Prevention.

15.2 Waste Streams Produced by this Method

The following waste stream is produced when this procedure is performed:

- Expired Standards; these standards are returned to the vendor for disposal.

## 16.0 REFERENCES

16.1 Compendium Method TO-15, "Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry", US EPA, January, 1999.

16.2 Compendium Method TO-14, "Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry", US EPA, January, 1999.

## 17.0 TABLES, DIAGRAMS & FLOWCHARTS

17.1 Table 1: *Target Analyte List*
17.2 Table 2: *Ion Abundance Criteria*
17.3 Table 3: *QC Summary and Recommended Corrective Action*

**Table 1: Target Analyte List, RL, Quantitation Ions, Internal Standard and Calibration Goup Assignments**

**Denotes TO-14 Target Analyte List*

*[1] TO-15 Target Analyte List*

| TO-14 | Analyte[1] | CAS No. | 6L RL (ppbv) | 1L RL (ppbv) | Quant Mass | Qualifier Mass | Qualifier Mass | ISTD Group | Cal Group |
|---|---|---|---|---|---|---|---|---|---|
| * | Dichlorodifluoromethane | 75-71-8 | 0.5 | 5 | 85 | 87 | | 1 | B |
| * | 1,2-Dichlorotetrafluoroethane | 76-14-2 | 0.2 | 2 | 85 | 135 | 87 | 1 | A |
| * | Chloromethane | 74-87-3 | 0.5 | 5 | 50 | 52 | | 1 | B |
| * | Vinyl Chloride | 75-01-4 | 0.2 | 2 | 62 | 64 | | 1 | A |
| | 1,3-Butadiene | 106-99-0 | 0.2 | 2 | 54 | 0 | | 1 | A |
| * | Bromomethane | 74-83-9 | 0.2 | 2 | 94 | 96 | | 1 | A |
| * | Chloroethane | 75-00-3 | 0.2 | 2 | 64 | 66 | | 1 | A |
| | Bromoethene | 593-60-2 | 0.2 | 2 | 106 | 108 | 81 | 1 | A |
| * | Trichlorofluoromethane | 75-69-4 | 0.2 | 2 | 101 | 103 | | 1 | A |
| * | Freon TF | 76-13-1 | 0.2 | 2 | 101 | 151 | 103 | 1 | A |
| * | 1,1-Dichloroethene | 75-35-4 | 0.2 | 2 | 96 | 61 | 63 | 1 | A |
| | Acetone | 67-64-1 | 5 | 50 | 43 | 58 | | 1 | C |
| | Isopropyl Alcohol | 67-63-0 | 5 | 50 | 45 | 43 | | 1 | C |
| | Carbon Disulfide | 75-15-0 | 0.5 | 5 | 76 | | | 1 | B |
| | 3-Chloropropene | 107-05-1 | 0.2 | 2 | 41 | 76 | | 1 | A |
| * | Methylene Chloride | 75-09-2 | 0.5 | 5 | 49 | 84 | 86 | 1 | B |
| | tert-Butyl Alcohol | 75-65-0 | 5 | 50 | 59 | 41 | 43 | 1 | C |
| | Methyl tert-Butyl Ether | 1634-04-4 | 0.5 | 5 | 73 | 43 | | 1 | B |
| | trans-1,2-Dichloroethene | 156-60-5 | 0.2 | 2 | 61 | 96 | | 1 | A |
| | n-Hexane | 110-54-3 | 0.2 | 2 | 57 | 86 | | 1 | A |
| * | 1,1-Dichloroethane | 75-34-3 | 0.2 | 2 | 63 | 65 | 83 | 1 | A |
| | 1,2-Dichloroethene (total) | 540-59-0 | 0.2 | 2 | 61 | 96 | | 1 | A |
| | Methyl Ethyl Ketone | 78-93-3 | 0.5 | 5 | 43 | 72 | | 1 | B |
| * | cis-1,2-Dichloroethene | 156-59-2 | 0.2 | 2 | 96 | 98 | | 1 | A |
| * | Chloroform | 67-66-3 | 0.2 | 2 | 83 | 85 | | 1 | A |
| | Tetrahydrofuran | 109-99-9 | 5 | 50 | 42 | 72 | | 2 | C |
| * | 1,1,1-Trichloroethane | 71-55-6 | 0.2 | 2 | 97 | 99 | 61 | 2 | A |
| | Cyclohexane | 110-82-7 | 0.2 | 2 | 84 | 56 | | 2 | A |
| * | Carbon Tetrachloride | 56-23-5 | 0.2 | 2 | 117 | 119 | | 2 | A |
| | 2,2,4-Trimethylpentane | 540-84-1 | 0.2 | 2 | 57 | 41 | 43 | 2 | A |
| * | Benzene | 71-43-2 | 0.2 | 2 | 78 | 77 | | 2 | A |
| * | 1,2-Dichloroethane | 107-06-2 | 0.2 | 2 | 62 | 98 | | 2 | A |
| | n-Heptane | 142-82-5 | 0.2 | 2 | 43 | 71 | | 2 | A |
| * | Trichloroethene | 79-01-6 | 0.2 | 2 | 95 | 130 | 132 | 2 | A |
| | Methyl Methacrylate | 80-62-6 | 0.5 | 5 | 69 | 41 | 39 | 2 | B |
| * | 1,2-Dichloropropane | 78-87-5 | 0.2 | 2 | 63 | 41 | | 2 | A |
| | 1,4-Dioxane | 123-91-1 | 5 | 50 | 88 | 58 | | 2 | C |
| | Bromodichloromethane | 75-27-4 | 0.2 | 2 | 83 | 85 | | 2 | A |
| * | cis-1,3-Dichloropropene | 10061-01-5 | 0.2 | 2 | 75 | 110 | | 2 | A |
| | Methyl Isobutyl Ketone | 108-10-1 | 0.5 | 5 | 43 | 58 | | 2 | B |
| * | Toluene | 108-88-3 | 0.2 | 2 | 92 | 91 | | 3 | A |
| * | trans-1,3-Dichloropropene | 10061-02-6 | 0.2 | 2 | 75 | 110 | | 2 | A |
| * | 1,1,2-Trichloroethane | 79-00-5 | 0.2 | 2 | 83 | 97 | 85 | 3 | A |
| * | Tetrachloroethene | 127-18-4 | 0.2 | 2 | 166 | 168 | 129 | 3 | A |

**Table 1 Continued**

| TO-14 | Analyte[1] | CAS No. | 6L RL (ppbv) | 1L RL (ppbv) | Quant Mass | Qualifier Mass | Qualifier Mass | ISTD Group | Cal Group |
|---|---|---|---|---|---|---|---|---|---|
| | Methyl Butyl Ketone | 591-78-6 | 0.5 | 5 | 43 | 58 | | 3 | B |
| | Dibromochloromethane | 124-48-1 | 0.2 | 2 | 129 | 127 | | 3 | A |
| * | 1,2-Dibromoethane | 106-93-4 | 0.2 | 2 | 107 | 109 | | 3 | A |
| * | Chlorobenzene | 108-90-7 | 0.2 | 2 | 112 | 77 | 114 | 3 | A |
| * | Ethylbenzene | 100-41-4 | 0.2 | 2 | 91 | 106 | | 3 | A |
| * | Xylene (m,p) | 1330-20-7 | 0.2 | 2 | 106 | 91 | | 3 | A |
| * | Xylene (o) | 95-47-6 | 0.2 | 2 | 106 | 91 | | 3 | A |
| * | Styrene | 100-42-5 | 0.2 | 2 | 104 | 78 | | 3 | A |
| | Xylene (total) | 1330-20-7 | 0.2 | 2 | 106 | 91 | | 3 | A |
| | Bromoform | 75-25-2 | 0.2 | 2 | 173 | 175 | 171 | 3 | E |
| * | 1,1,2,2-Tetrachloroethane | 79-34-5 | 0.2 | 2 | 83 | 131 | 85 | 3 | A |
| | 4-Ethyltoluene | 622-96-8 | 0.2 | 2 | 105 | 120 | | 3 | A |
| * | 1,3,5-Trimethylbenzene | 108-67-8 | 0.2 | 2 | 105 | 120 | | 3 | A |
| | 2-Chlorotoluene | 95-49-8 | 0.2 | 2 | 91 | 63 | | 3 | A |
| * | 1,2,4-Trimethylbenzene | 95-63-6 | 0.2 | 2 | 105 | 120 | | 3 | A |
| * | 1,3-Dichlorobenzene | 541-73-1 | 0.2 | 2 | 146 | 111 | 148 | 3 | A |
| * | 1,4-Dichlorobenzene | 106-46-7 | 0.2 | 2 | 146 | 111 | 148 | 3 | A |
| * | 1,2-Dichlorobenzene | 95-50-1 | 0.2 | 2 | 146 | 111 | 148 | 3 | A |
| * | 1,2,4-Trichlorobenzene | 120-82-1 | 0.5 | 5 | 180 | 182 | | 3 | B |
| * | Hexachlorobutadiene | 87-68-3 | 0.2 | 2 | 225 | 223 | | 3 | A |
| | Naphthalene | 91-20-3 | 0.5 | 5 | 128 | | | 3 | D |
| | **Internal Standards** | | | | | | | | |
| * | Bromochloromethane | 74-97-5 | NA | NA | 128 | 49 | 130 | 1 | NA |
| * | 1,4-Difluorobenzene | 540-36-3 | NA | NA | 114 | | | 2 | NA |
| * | Chlorobenzene-d5 | 3114-55-4 | NA | NA | 117 | | | 3 | NA |

**Table 2: BFB Tune Criteria**

| BFB Key Ions and Ion Abundance Criteria | |
|---|---|
| **Mass** | **Ion Abundance Criteria** |
| 50 | 8.0 to 40.0 percent of mass 95 |
| 75 | 30.0 to 66.0 percent of mass 95 |
| 95 | Base Peak, 100 percent relative abundance |
| 96 | 5.0 to 9.0 percent of mass 95 |
| 173 | Less than 2.0 percent of mass 174 |
| 174 | 50.0 to 120.0 percent of mass 95 |
| 175 | 4.0 to 9.0 percent of mass 174 |
| 176 | 93.0 to 101.0 percent of mass 174 |
| 177 | 5.0 to 9.0 percent of mass 176 |

**Table 3: QC Summary and Recommended Corrective Action (EPA TO-15, EPA TO-14)**

| QC Check | Minimum Frequency | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| BFB Tune | Prior to calibration and every 24 hours during sample analysis | See Table 2 | Correct problem, reanalyze |
| ICAL | As Needed | %RSD for each target analyte ≤ 30% with at most two exceptions up to 40%* | Correct problem, repeat calibration. |
| ICV/LCS | ICV: After each ICAL<br>LCS: Per analytical batch or every 20 samples, whichever is more frequent | %R (70-130) | ICV: Correct problem, reverify second source standard. If that fails, repeat calibration.<br>LCS: Correct problem, reanalyze LCS and all samples in associated batch. Flag data. |
| LCSD | Per analytical batch or every 20 samples, whichever is more frequent | %R (70-130)<br>RPD ≤ 25 | Correct problem, reanalyze LCSD and all samples in associated batch. Flag data. |
| CCV | Daily, before sample analysis | %D for each target analyte ≤ 30% | Correct problem, reanalyze, repeat initial calibration. |
| Method Blank | One per analytical batch or every 20 samples, whichever is more frequent | No analytes > RL<br>DoD: ½ RL | Reanalyze all samples associated with method blank; Flag data. |
| Internal Standards | Added to every calibration standard and field and QC check sample. | ± 40% area response from last acceptable calibration<br>RT± .33min (20 seconds) from last acceptable calibration. | Reanalyze |

## USEPA Method TO-15 Reporting Limits

### TO-15 Target Compounds[1], RLs

| Compound | CAS Number | Molecular Weight | Reporting Limit ppbv | Reporting Limit ug/m$^3$ | Full TO15 |
|---|---|---|---|---|---|
| Acetone (2-propanone) | 67-64-1 | 58.08 | 5.0 | 12 | X |
| Benzene | 71-43-2 | 78.11 | 0.20 | 0.64 | X |
| Bromodichloromethane | 75-27-4 | 163.83 | 0.20 | 1.3 | X |
| Bromoethene | 593-60-2 | 106.96 | 0.20 | 0.87 | X |
| Bromoform | 75-25-2 | 252.75 | 0.20 | 2.1 | X |
| Bromomethane (Methyl bromide) | 74-83-9 | 94.95 | 0.20 | 0.78 | X |
| 1,3-Butadiene | 106-99-0 | 60.14 | 0.50 | 1.23 | X |
| 2-Butanone (Methyl ethyl ketone) | 78-93-3 | 72.11 | 0.50 | 1.5 | X |
| Carbon disulfide | 75-15-0 | 76.14 | 0.50 | 1.6 | X |
| Carbon tetrachloride | 56-23-5 | 153.84 | 0.20 | 1.3 | X |
| Chlorobenzene | 108-90-7 | 112.56 | 0.20 | 0.92 | X |
| Chloroethane | 75-00-3 | 64.52 | 0.50 | 1.32 | X |
| Chloroform | 67-66-3 | 119.39 | 0.20 | 0.98 | X |
| Chloromethane (Methyl chloride) | 74-87-3 | 50.49 | 0.20 | 0.41 | X |
| 3-Chloropropene (allyl chloride) | 107-05-1 | 76.53 | 0.50 | 1.57 | X |
| 2-Chlorotoluene (o-Chlorotoluene) | 95-49-8 | 126.59 | 0.20 | 1.04 | X |
| Cyclohexane | 110-82-7 | 84.16 | 0.20 | 0.69 | X |
| Dibromochloromethane | 124-48-1 | 242.74 | 0.20 | 2.0 | X |
| 1,2-Dibromoethane | 106-93-4 | 187.88 | 0.20 | 1.5 | X |
| 1,2-Dichlorobenzene | 95-50-1 | 147.01 | 0.20 | 1.2 | X |
| 1,3-Dichlorobenzene | 541-73-1 | 147.01 | 0.20 | 1.2 | X |
| 1,4-Dichlorobenzene | 106-46-7 | 147.01 | 0.20 | 1.2 | X |
| Dichlorodifluoromethane (Freon 12) | 75-71-8 | 120.92 | 0.50 | 2.47 | X |
| 1,1-Dichloroethane | 75-34-3 | 98.97 | 0.20 | 0.81 | X |
| 1,2-Dichloroethane | 107-06-2 | 98.96 | 0.20 | 0.81 | X |
| 1,1-Dichloroethene | 75-35-4 | 96.95 | 0.20 | 0.79 | X |
| 1,2-Dichloroethene (cis) | 156-59-2 | 96.95 | 0.20 | 0.79 | X |
| 1,2-Dichloroethene (trans) | 156-60-5 | 96.95 | 0.20 | 0.79 | X |
| 1,2-Dichloropropane | 78-87-5 | 112.99 | 0.20 | 0.92 | X |
| cis-1,3-Dichloropropene | 10061-01-5 | 110.98 | 0.20 | 0.91 | X |
| trans-1,3-Dichloropropene | 10061-02-6 | 110.98 | 0.20 | 0.91 | X |
| 1,2-Dichlorotetrafluoroethane (Freon 114) | 76-14-2 | 170.93 | 0.20 | 1.4 | X |
| Ethylbenzene | 100-41-4 | 106.16 | 0.20 | 0.87 | X |
| 4-Ethyltoluene (p-Ethyltoluene) | 622-96-8 | 120.2 | 0.20 | 0.98 | X |
| n-Heptane | 142-82-5 | 101.2 | 0.20 | 0.83 | X |
| Hexachlorobutadiene | 87-68-3 | 260.76 | 0.20 | 2.1 | X |
| n-Hexane | 110-54-3 | 86.18 | 0.50 | 1.76 | X |
| Methylene chloride | 75-09-2 | 84.94 | 0.50 | 1.7 | X |
| 4-Methyl-2-pentanone (MIBK) | 108-10-1 | 100.16 | 0.50 | 2.05 | X |
| MTBE (Methyl tert-butyl ether) | 1634-04-4 | 88.15 | 0.50 | 1.8 | X |
| Styrene | 100-42-5 | 104.14 | 0.20 | 0.85 | X |
| Tertiary butyl alcohol (TBA) | 75-65-0 | 74.12 | 5.0 | 15 | X |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 167.86 | 0.20 | 1.4 | X |
| Tetrachloroethene (PCE) | 127-18-4 | 165.85 | 0.20 | 1.4 | X |
| Toluene | 108-88-3 | 92.13 | 0.20 | 0.75 | X |
| 1,2,4-Trichlorobenzene | 120-82-1 | 181.46 | 0.50 | 3.7 | X |
| 1,1,1-Trichloroethane | 71-55-6 | 133.42 | 0.20 | 1.1 | X |
| 1,1,2-Trichloroethane | 79-00-5 | 133.42 | 0.20 | 1.1 | X |
| 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon TF) | 76-13-1 | 187.38 | 0.20 | 1.5 | X |
| Trichloroethene (TCE) | 79-01-6 | 131.4 | 0.20 | 1.07 | X |
| Trichlorofluoromethane (Freon 11) | 75-69-4 | 137.38 | 0.20 | 1.1 | X |
| 1,2,4-Trimethylbenzene | 95-63-6 | 120.19 | 0.20 | 0.98 | X |
| 1,3,5-Trimethylbenzene | 108-67-8 | 120.19 | 0.20 | 0.98 | X |
| 2,2,4-Trimethylpentane | 540-84-1 | 132.38 | 0.20 | 1.08 | X |
| Vinyl chloride | 75-01-4 | 62.5 | 0.20 | 0.51 | X |
| Xylenes (m&p) | 1330-20-7 | 106.16 | 0.50 | 2.17 | X |
| Xylenes (o) | 95-47-6 | 106.16 | 0.20 | 0.87 | X |
| 1,2-Dichloroethene (total) | 540-59-0 | 96.95 | 0.20 | 0.79 | X |
| 1,4-Dioxane | 123-91-1 | 88.11 | 5.0 | 18 | X |
| Isopropyl Alcohol | 67-63-0 | 61.09 | 5.0 | 12.5 | X |
| Methyl Butyl Ketone | 591-78-6 | 100.16 | 0.50 | 2.05 | X |
| Methyl methacrylate (upon request only) | 80-62-6 | 100.1 | 0.50 | 2.05 | X |
| Naphthalene (upon request only) | 91-20-3 | 142.2 | 0.50 | 2.9 | X |
| Tetrahydrofuran | 109-99-9 | 72.11 | 5.0 | 15 | X |

[1]NJ compounds have NJ-assigned compound names

## TO-15 Target Compounds[1], RLs

| | Compound | CAS Number | Molecular Weigth | Reporting Limit ppbv | Reporting Limit ug/m$^3$ | TO15 |
|---|---|---|---|---|---|---|
| 1 | 1,1,1-Trichloroethane | 71-55-6 | 133.42 | 0.20 | 1.1 | X |
| 2 | 1,1,2,2-Tetrachloroethane | 79-34-5 | 167.86 | 0.20 | 1.4 | X |
| 3 | 1,1,2-Trichloroethane | 79-00-5 | 133.42 | 0.20 | 1.1 | X |
| 4 | 1,1-Dichloroethane | 75-34-3 | 98.97 | 0.20 | 0.81 | X |
| 5 | 1,1-Dichloroethene | 75-35-4 | 96.95 | 0.20 | 0.79 | X |
| 6 | 1,2-Dichloroethane | 107-06-2 | 98.96 | 0.20 | 0.81 | X |
| 7 | 1,2-Dichloroethene (total) | 540-59-0 | 96.95 | 0.20 | 0.79 | X |
| 8 | cis-1,2-Dichloroethene | 156-59-2 | 96.95 | 0.20 | 0.79 | X |
| 9 | Tetrachloroethene (PCE) | 127-18-4 | 165.85 | 0.20 | 1.4 | X |
| 10 | trans-1,2-Dichloroethene | 156-60-5 | 96.95 | 0.20 | 0.79 | X |
| 11 | Trichloroethene (TCE) | 79-01-6 | 131.4 | 0.20 | 1.07 | X |
| 12 | Vinyl chloride | 75-01-4 | 62.5 | 0.20 | 0.51 | X |

# USEPA. 2002. STANDARD OPERATING PROCEDURE (SOP) FOR INSTALLATION OF SUB-SLAB VAPOR PROBES

Draft

# Standard Operating Procedure (SOP) for Installation of Sub-Slab Vapor Probes and Sampling Using EPA Method TO-15 to Support Vapor Intrusion Investigations

Dominic DiGiulio, Ph.D.
U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Ground-Water and Ecosystem Restoration Division
Ada, Oklahoma

phone: 580-436-8605
e-mail: digiulio.dominic@epa.gov

## Background

Vapor intrusion is defined as vapor phase migration of volatile organic and/or inorganic compounds into occupied buildings from underlying contaminated ground water and/or soil. Until recently, this transport pathway was not routinely considered in RCRA, CERCLA, or UST investigations. Therefore the number of buildings or homes where vapor intrusion has occurred or is occurring is undefined. However, considering the vast number of current and former industrial, commercial, and waste processing facilities in the United States capable of causing volatile organic or inorganic ground-water or soil contamination, contaminant exposure via vapor intrusion could pose a significant risk to the public. Also, consideration of this transport pathway may necessitate review of remedial decisions at RCRA and CERCLA sites as well as implementation of risk-reduction technologies at Brownsfield sites where future development and subsequent potential exposure may occur. EPA's Office of Solid Waste and Emergency Response (OSWER) recently (2002) developed guidance to facilitate assessment of vapor intrusion at sites regulated by RCRA and CERCLA where halogenated organic compounds constitute the bulk of risk to human health. EPA's Office of Underground Storage Tanks (OUST) is considering modifying this guidance to include underground storage tank sites where petroleum compounds primarily determine risk and biodegradation in subsurface media may be a dominant fate process.

The OSWER guidance recommends indoor air and sub-slab gas sampling in potentially affected buildings at sites containing elevated levels of soil-gas and ground-water contamination. To support the guidance and improve site-characterization and data interpretation methods to assess vapor intrusion, EPA's Office or Research and Development is developing a protocol for sub-slab gas sampling. When used in conjunction with indoor air, outdoor air, and soil gas and/or ground-water sampling, sub-slab gas sampling can be used to differentiate indoor and outdoor sources of volatile organic and/or inorganic compounds from compounds emanating from contaminated subsurface media. This information can then be used to assess the need for sub-slab depressurization or other risk-reduction technologies to reduce present or potential future indoor air contamination due to vapor intrusion.

## Sub-Slab Vapor Probe Construction and Installation

1. Prior to drilling holes in a foundation or slab, contact local utility companies to identify and mark utilities coming into the building from the outside (e.g., gas, water, sewer, refrigerant, and electrical lines). Consult with a local electrician and plumber to identify the location of utilities inside the building.

2. Prior to fabrication of sub-slab vapor probes, drill a pilot hole to assess the thickness of a slab. As illustrated in **Figure 1**, use a rotary hammer drill to create a "shallow" (e.g., 2.5 cm or 1 in) "outer" hole (e.g., 2.2 cm or 7/8 in diameter) that partially penetrates the slab. Use a small portable vacuum cleaner to remove cuttings from the hole if penetration has not occurred. Removal of cuttings in this manner in a competent slab will not compromise sampling because of lack of pneumatic communication between sub-slab material and the source of vacuum.

3. Then use the rotary hammer drill to create a smaller diameter "inner" hole (e.g., 0.8 cm or 5/16 in) through the remainder of the slab and some depth (e.g., 7 to 8 cm or 3 in) into sub-slab material. **Figure 2** illustrates the appearance of "inner" and "outer" holes. Drilling into sub-slab material will create an open cavity which will prevent obstruction of

probes during sampling by small pieces of gravel.

4. The basic design of a sub-slab vapor probe is illustrated in **Figure 3.** Once the thickness of the slab is known, tubing should be cut to ensure that probes "float" in the slab to avoid obstruction of the probe with sub-slab material. Construct sub-slab vapor probes from small diameter (e.g., 0.64 cm or 1/4 in OD x 0.46 cm or 0.18 in ID) chromatography grade 316 stainless steel tubing and stainless-steel compression to thread fittings (e.g., 0.64 cm or 1/4 in OD x 0.32 cm or 1/8 in NPT Swagelok female thread connectors) as illustrated in **Figure 4.** Use of stainless-steel materials to ensure that construction materials are not a source of VOCs.

5. Set sub-slab vapor probes in holes. As illustrated in **Figure 5**, the top of the probes should be completed flush with the slab and have recessed stainless steel or brass plugs so as not interfere with day-to-day use of buildings. Mix a quick-drying portland cement which expands upon drying (to ensure a tight seal) with water to form a slurry and inject or push into the annular space between the probe and outside of the "outer" hole. Allow cement to cure for at least 24 hours prior to sampling.

6. Install at least 3 sub-slab vapor probes in each residence. As illustrated in **Figure 6,** create a schematic identifying the location of each sub-slab probe.

**Sub-Slab Sampling**

1. Connect dedicated a stainless-steel fitting and tubing (e.g., 1/8 in NPT to 1/4 in tube Swagelok fitting and 30 cm or 1 ft of 1/4 in I.D. Teflon tubing to a sub-slab vapor probe as illustrated in **Figure 7**. Use of dedicated fitting and tubing will avoid cross-contamination issues.

2. Connect the Teflon tubing to 1/4" ID Masterflex (e.g., 1.4 in ID high performance Tygon LFL) tubing and a peristaltic pump and 1-L Tedlar bag as illustrated in **Figure 8.** Use of a peristaltic pump will ensure that sampled air does not circulate through a pump causing potential cross contamination and leakage.

3. Purge vapor probe by filling two dedicated 1-L Tedlar bags. The internal volume of sub-slab probes is insignificant (< 5 $cm^3$). A purge volume of 2 L was chosen based on the assumption of a 0.64 cm (1/4") air space beneath a slab and an affected sample diameter of 0.61 m (2 ft).

4. Use a portable landfill gas meter to analyze for $O_2$, $CO_2$ and $CH_4$ in Tedlar bags as illustrated in **Figure 9.**

5. Collect sub-slab vapor samples in evacuated 10% or 100% certified 1-L Summa polished canisters and dedicated particulate filters as illustrated in **Figure 10.** Check vacuum in canisters prior to sampling. Sampling will cease when canister pressure reaches atmospheric pressure. Submit canisters to a commercial laboratory for analysis by EPA Method TO-15.

6. Collect at least one duplicate sub-slab sample per building using dedicated stainless-steel tubing as illustrated in **Figure 11.**

**Figure 1.** Drilling through a slab

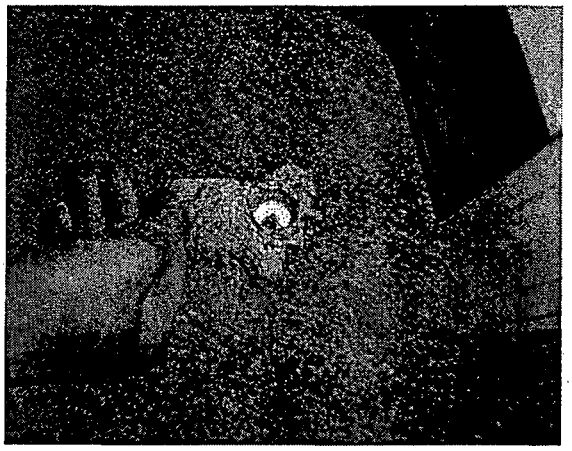


**Figure 2.** "inner and "outer

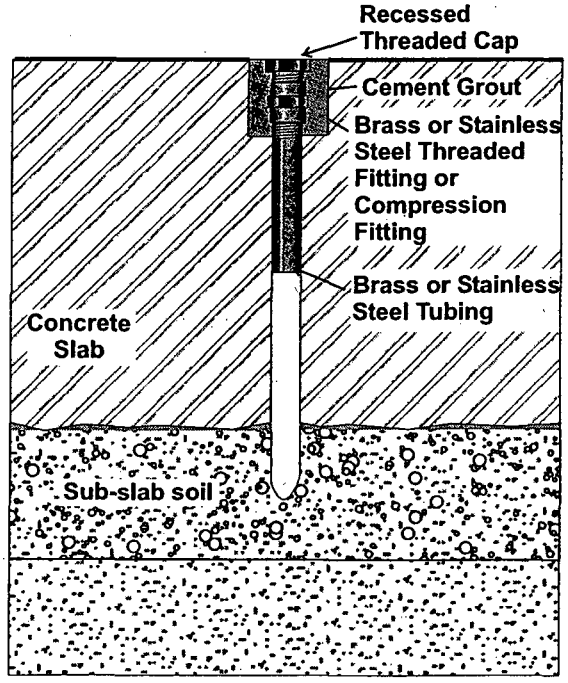



**Figure 3.** General schematic of sub-slab vapor probe

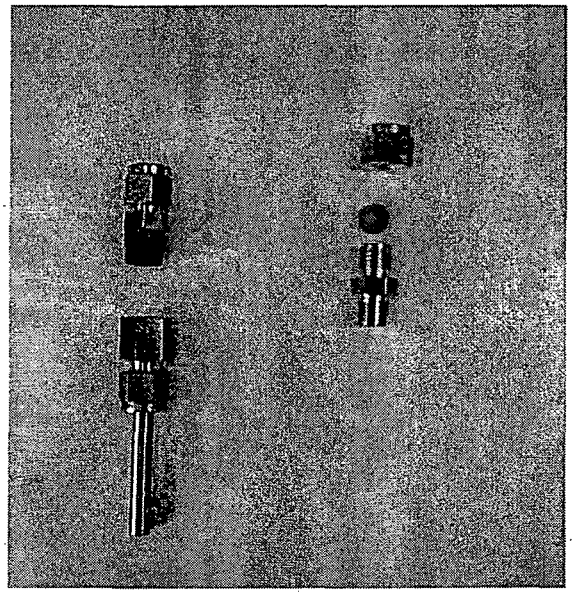


**Figure 4.** Stainless steel sub-slab vapor probe components

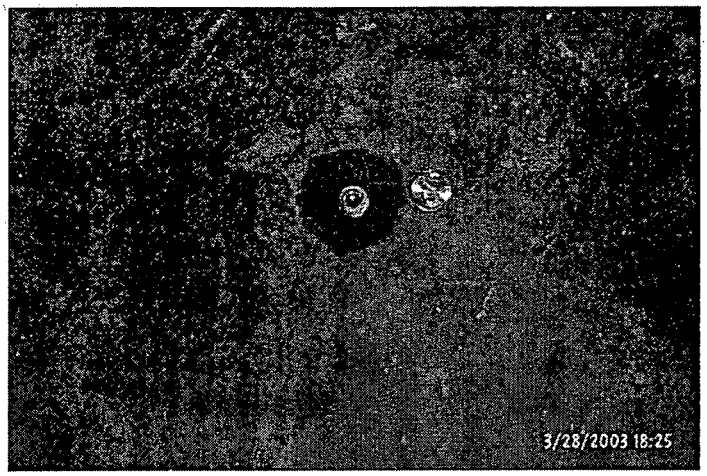



**Figure 5.** Competed vapor probe installation

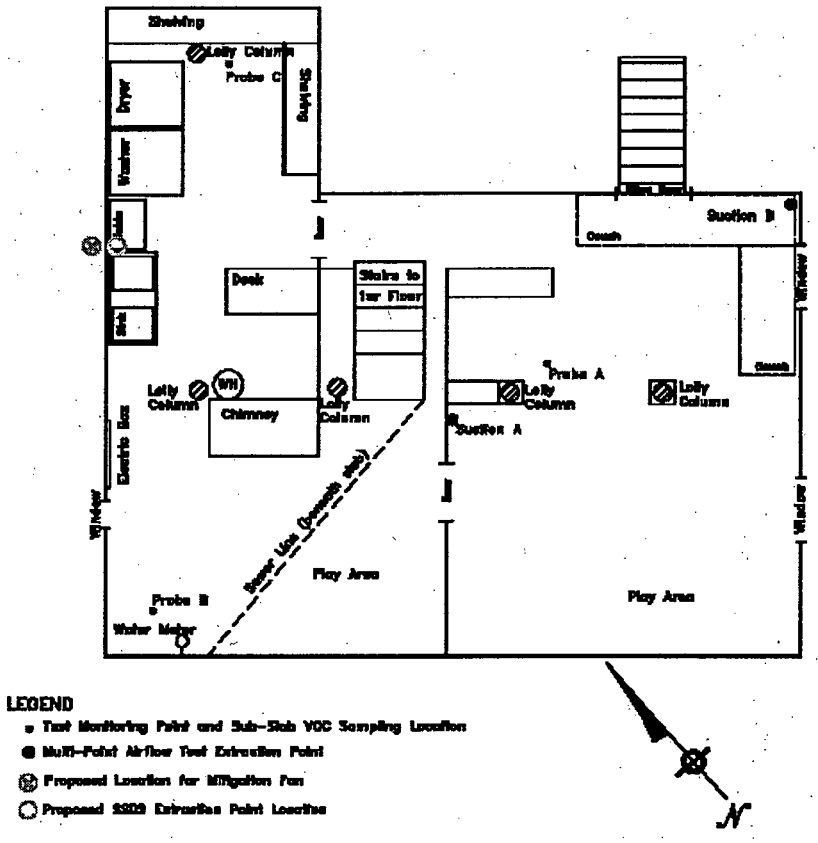



**Figure 6.** Schematic illustration location of vapor probes in a basement

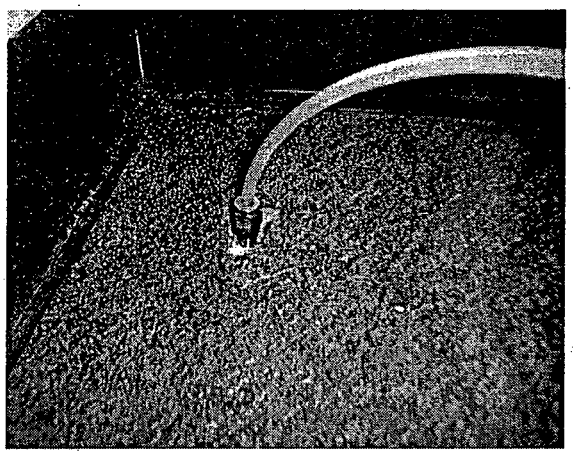


**Figure 7.** Compression fitting to probe

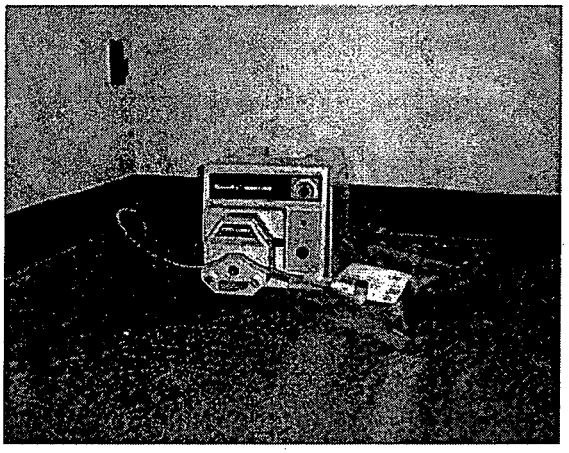


**Figure 8.** Purge prior to sampling

**Figure 9.** Analysis of O2, CO2, and CH4

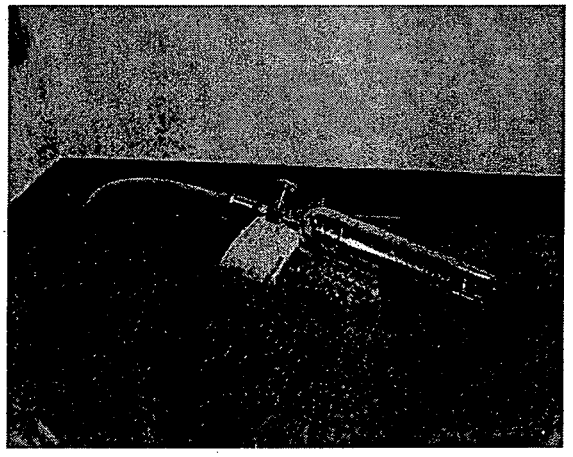


**Figure 10.** Sampling in 1-L evacuated canister for TO-15 analysis

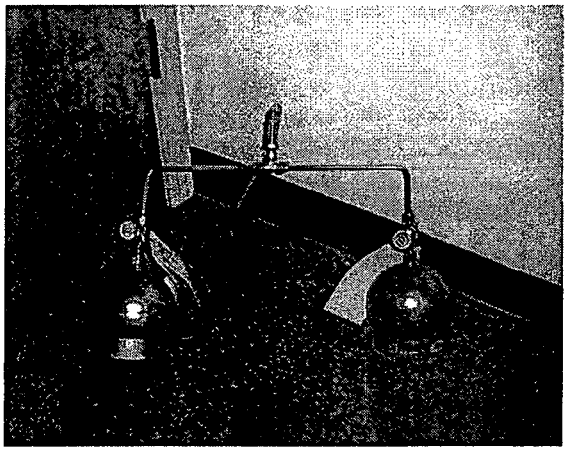


**Figure 11.** Collection of duplicate sample

# USEPA. 1996. ENVIRONMENTAL RESPONSE TEAM (ERT) STANDARD OPERATING PROCEDURE (SOP) # 2042

# SOIL GAS SAMPLING

SOP#: 2042
DATE: 06/01/96
REV. #: 0.0

## 1.0 SCOPE AND APPLICATION

Soil gas monitoring provides a quick means of waste site evaluation. Using this method, underground contamination can be identified, and the source, extent, and movement of the pollutants can be traced.

This standard operating procedure (SOP) outlines the methods used by U.S. EPA/ERT in installing soil gas wells; measuring organic vapor levels in the soil gas using a Photoionization Detector (PID), Flame Ionization Detector (FID) and/or other air monitoring devices; and sampling the soil gas using Tedlar bags, Tenax sorbent tubes, and/or Summa canisters.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

A 3/8" diameter hole is driven into the ground to a depth of four to five feet using a commercially available slam bar. Soil gas can also be sampled at other depths by the use of a longer bar or bar attachments. A 1/4" O.D. stainless steel probe is inserted into the hole. The hole is then sealed around the top of the probe using modeling clay. The gas contained in the interstitial spaces of the soil is sampled by pulling the sample through the probe using an air sampling pump. The sample may be stored in Tedlar bags, drawn through sorbent cartridges, or analyzed directly using a direct reading instrument. The air sampling pump is not used for Summa canister sampling of soil gas. Sampling is achieved by soil gas equilibration with the evacuated Summa canister.

Other field air monitoring devices, such as the combustible gas indicator (MSA CGI/02 Meter, Model 260) and the Organic Vapor Analyzer (Foxboro OVA, Model 128), can also be used dependent on specific site conditions. Measurement of soil temperature using a temperature probe may also be desirable. Bagged samples are usually analyzed in a field laboratory using a portable Photovac GC.

Power driven sampling probes may be utilized when soil conditions make sampling by hand unfeasible (i.e., frozen ground, very dense clays, pavement, etc.). Commercially available soil gas sampling probes (hollow, 1/2 = O.D. steel probes) can be driven to the desired depth using a power hammer (e.g., Bosch Demolition Hammer or Geoprobe™). Samples can be drawn through the probe itself, or through Teflon tubing inserted through the probe and attached to the probe point. Samples are collected and analyzed as described above.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

### 3.1 Tedlar Bags

Soil gas samples are generally contained in 1.0-L Tedlar bags. Bagged samples are best stored in dark plastic bags placed in coolers to protect the bags from any damage that may occur in the field or in transit. In addition, coolers insure the integrity of the samples by keeping them at a cool temperature and out of direct sunlight. Samples should be analyzed as soon as possible, preferably within 24 - 48 hours.

### 3.2 Tenax Tubes

Bagged samples can also be drawn onto Tenax or

other sorbent tubes to undergo lab GC/MS analysis. If Tenax tubes are to be utilized, special care must be taken to avoid contamination. Handling of the tubes should be kept to a minimum and only while wearing nylon or other lint-free gloves. After sampling, each tube should be stored in a clean, sealed culture tube; the ends packed with clean glass wool to protect the sorbent tube from breakage. The culture tubes should be kept cool and wrapped in aluminum foil to prevent any photodegradation of samples (see Section 7.4.).

### 3.3 Summa Canisters

The Summa canisters used for soil gas sampling have a 6 liter sample capacity and are certified clean by GC/MS analysis before being utilized in the field. After sampling is completed, they are stored and shipped in travel cases.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

### 4.1 PID Measurements

A number of factors can affect the response of a PID (such as the HNu PI 101). High humidity can cause lamp fogging and decreased sensitivity. This can be significant when soil moisture levels are high, or when a soil gas well is actually in groundwater. High concentrations of methane can cause a downscale deflection of the meter. High and low temperature, electrical fields, FM radio transmission, and naturally occurring compounds, such as terpenes in wooded areas, will also affect instrument response.

Other field screening instruments can be affected by interferences. Consult the manufacturers manuals.

### 4.2 FID Measurements

A number of factors can affect the response of an FID (such as the OVA model 128). High humidity can cause the FID to flame out or not ignite at all. This can be significant when soil moisture levels are high, or when a soil gas well is actually in groundwater. The FID can only read organic based compounds (they must contain carbon in the molecular structure). The FID also responds poorly to hydrocarbons and halogenated hydrocarbons (such as gasoline, propane fuel). High and low temperature, electrical fields and FM radio transmission will also affect instrument response.

### 4.3 Factors Affecting Organic Concentrations in Soil Gas

Concentrations in soil gas are affected by dissolution, adsorption, and partitioning. Partitioning refers to the ratio of component found in a saturated vapor above an aqueous solution to the amount in the solution; this can, in theory, be calculated using the Henry's Law constants. Contaminants can also be adsorbed onto inorganic soil components or "dissolved" in organic components. These factors can result in a lowering of the partitioning coefficient.

Soil "tightness" or amount of void space in the soil matrix, will affect the rate of recharging of gas into the soil gas well.

Existence of a high, or perched, water table, or of an impermeable underlying layer (such as a clay lens or layer of buried slag) may interfere with sampling of the soil gas. Knowledge of site geology is useful in such situations, and can prevent inaccurate sampling.

### 4.4 Soil Probe Clogging

A common problem with this sampling method is soil probe clogging. A clogged probe can be identified by using an in-line vacuum gauge or by listening for the sound of the pump laboring. This problem can usually be eliminated by using a wire cable to clear probe (see Section 7.1.3.).

### 4.5 Underground Utilities

Prior to selecting sample locations, an underground utility search is recommended. The local utility companies can be contacted and requested to mark the locations of their underground lines. Sampling plans can then be drawn up accordingly. Each sample location should also be screened with a metal detector or magnetometer to verify that no underground pipes or drums exist.

## 5.0 EQUIPMENT/APPARATUS

### 5.1 Slam Bar Method

- Slam Bar (1 per sampling team).
- Soil gas probes, stainless steel tubing, 1/4" O.D., 5 ft length.
- Flexible wire or cable used for clearing the

tubing during insertion into the well.
- "Quick Connect" fittings to connect sampling probe tubing, monitoring instruments, and Gilian pumps to appropriate fittings on vacuum box.
- Modeling clay.
- Vacuum box for drawing a vacuum around Tedlar bag for sample collection (1 per sampling team).
- Gilian pump Model HFS113A adjusted to approximately 3.0 L/min (1 to 2 per sample team).
- 1/4" Teflon tubing, 2 ft to 3 ft lengths, for replacement of contaminated sample line.
- 1/4" Tygon tubing, to connect Teflon tubing to probes and quick connect fittings.
- Tedlar bags, 1.0 L, at least 1 bag per sample point.
- Soil Gas Sampling labels, field data sheets, logbook, etc.
- PID/FID, or other field air monitoring devices, (1 per sampling team).
- Ice chest, for carrying equipment and for protection of samples (2 per sampling team).
- Metal detector or magnetometer, for detecting underground utilities/pipes/drums (1 per sampling team).
- Photovac GC, for field-lab analysis of bagged samples.
- Summa canisters (plus their shipping cases) for sample, storage and transportation.
- Large dark plastic garbage bags

## 5.2 Power Hammer Method

- Bosch demolition hammer.
- 1/2" O.D. steel probes, extensions, and points.
- Dedicated aluminum sampling points.
- Teflon tubing, 1/4".
- "Quick Connect" fittings to connect sampling probe tubing, monitoring instruments, and Gilian pumps to appropriate fittings on vacuum box.
- Modeling clay.
- Vacuum box for drawing a vacuum around Tedlar bag for sample collection (1 per sampling team).
- Gilian pump Model HFS113A adjusted to approximately 3.0 L/min (1 to 2 per sample team).
- 1/4" Teflon tubing, 2 ft to 3 ft lengths, for replacement of contaminated sample line.
- 1/4" Tygon tubing, to connect Teflon tubing to probes and quick connect fittings.
- Tedlar bags, 1.0 L, at least 1 bag per sample point.
- Soil Gas Sampling labels, field data sheets, logbook, etc.
- HNu Model P1101, or other field air monitoring devices, (1 per sampling team).
- Ice chest, for carrying equipment and for protection of samples (2 per sampling team).
- Metal detector or magnetometer, for detecting underground utilities/pipes/drums (1 per sampling team).
- Photovac GC, for field-lab analysis of bagged samples.
- Summa canisters (plus their shipping cases) for sample, storage and transportation.
- Generator w/extension cords.
- High lift jack assembly for removing probes.

## 5.3 Geoprobe™ Method

The Geoprobe is a hydraulically-operated sampling device mounted in a customized four-wheel drive vehicle. The sampling device can be deployed from the truck and positioned over a sample location. The base of the sampling device is positioned on the ground. The weight of the vehicle is hydraulically raised on the base. As the weight of the vehicle is transferred to the probe, the probe is pushed into the ground. A built-in hammer mechanism allows the probe to be driven past some dense stratigraphic horizons. When the probe reaches the sample depth, up to 50 feet under favorable geologic situations, samples can be collected.

Soil gas can be collected from specific depths in two general ways. One method involves withdrawing a sample directly from the probe rods, after evacuating a sufficient volume of air from the probe rods. The other method involves collecting a sample through tubing attached by an adaptor to the bottom probe rod section. Correctly used, this method provides more reliable results. Manufacturer's instructions and the SOP for the Model 5400 Geoprobe™ Operation should be followed when using this method.

## 6.0 REAGENTS

- PID/FID or calibration gases for field air monitoring devices (such as methane and

isobutylene).

- Deionized organic-free water, for decontamination.
- Methanol, HPLC grade, for decontamination.
- Ultra-zero grade compressed air, for field blanks.
- Standard gas preparations for Photovac GC calibration and Tedlar bag spikes.
- Propane Torch (for decontamination of steel probes)

# 7.0 PROCEDURES

## 7.1 Soil Gas Well Installation

1. Initially a hole slightly deeper than the desired depth is made. For sampling up to 5 feet, a 5-ft single piston slam bar is used. For deeper depths, a piston slam bar with threaded 4-foot-long extensions can be used. Other techniques can be used, so long as holes are of narrow diameter and no contamination is introduced.

2. After the hole is made, the slam bar is carefully withdrawn to prevent collapse of the walls of the hole. The soil gas probe is then inserted.

3. It is necessary to prevent plugging of the probe, especially for deeper holes. A metal wire or cable, slightly longer than the probe, is placed in the probe prior to inserting into the hole. The probe is inserted to full depth, then pulled up three to six inches, then cleared by moving the cable up and down. The cable is removed before sampling.

4. The top of the sample hole is sealed at the surface against ambient air infiltration by using modeling clay molded around the probe at the surface of the hole.

5. If conditions preclude hand installation of the soil gas wells, the power driven system may be employed. The generator powered demolition hammer is used to drive the probe to the desired depth (up to 12 Ft may be attained with extensions). The probe is pulled up 1-3 inches if the retractable point is used. No clay is needed to seal the hole. After sampling, the probe is retrieved using the high lift jack assembly.

6. If semi-permanent soil gas wells are required, the dedicated aluminum probe points are used. These points are inserted into the bottom of the power driven probe and attached to the Teflon tubing. The probe is inserted as in step 5. When the probe is removed, the point and Teflon tube remain in the hole, which may be sealed by backfilling with clean sand, soil, or bentonite.

## 7.2 Screening with Field Instruments

1. The well volume must be evacuated prior to sampling. Connect the Gilian pump, adjusted to 3.0 L/min, to the sample probe using a section of Teflon tubing as a connector. The pump is turned on, and a vacuum is pulled through the probe for approximately 15 seconds. Longer time is required for sample wells of greater depths.

2. After evacuation, the monitoring instrument(s) (i.e. HNu or OVA) is connected to the probe using a Teflon connector. When the reading is stable, or peaks, the reading is recorded on soil gas data sheets.

3. Of course, readings may be above or below the range set on the field instruments. The range may be reset, or the response recorded as a greater than or less than figure. Recharge rate of the well with soil gas must be considered when resampling at a different range setting.

## 7.3 Tedlar Bag Sampling

1. Follow step 7.2.1 to evacuate well volume. If air monitoring instrument screening was performed prior to sample taking, evacuation is not necessary.

2. Use the vacuum box and sampling train (Figure 1) to take the sample. The sampling train is designed to minimize the introduction of contaminants and losses due to adsorption. All wetted parts are either Teflon or stainless steel. The vacuum is drawn indirectly to avoid contamination from sample pumps.

3. The Tedlar bag is placed inside the vacuum box, and attached to the sampling port. The sample probe is attached to the sampling port via Teflon tubing and a "Quick Connect" fitting.

4. A vacuum is drawn around the outside of the bag, using a Gilian pump connected to the vacuum box evacuation port, via Tygon tubing and a "Quick Connect" fitting. The vacuum causes the bag to inflate, drawing the sample.

5. Break the vacuum by removing the Tygon line from the pump. Remove the bagged sample from the box and close valve. Record data on data sheets or in logbooks. Record the date, time, sample location ID, and the PID/FID instrument reading(s) on sample bag label.

CAUTION: Labels should not be pasted directly onto the bags, nor should bags be labeled directly using a marker or pen. Inks and adhesive may diffuse through the bag material, contaminating the sample. Place labels on the edge of the bags, or tie the labels to the metal eyelets provided on the bags. Markers with inks containing volatile organics (i.e., permanent ink markers) should not be used.

Chain of Custody Sheets must accompany all samples submitted to the field laboratory for analysis.

## 7.4 Tenax Tube Sampling

Samples collected in Tedlar bags may be adsorbed onto Tenax tubes for further analysis by GC/MS.

### 7.4.1 Additional Apparatus

A. Syringe with a luer-lock tip capable of drawing a soil gas or air sample from a Tedlar bag onto a Tenax/CMS sorbent tube. The syringe capacity is dependent upon the volume of sample begin drawn onto the sorbent tube.

B. Adapters for fitting the sorbent tube between the Tedlar bag and the sampling syringe. The adapter attaching the Tedlar bag to the sorbent tube consists of a reducing union (1/4" to 1/16" O.D. -- Swagelok cat. # SS-400-6-ILV or equivalent) with a length of 1/4" O.D. Teflon tubing replacing the nut on the 1/6" (Tedlar bag) side. A 1/4" I.D. silicone O-ring replaces the ferrules in the nut on the 1/4" (sorbent tube) side of the union.

The adapter attaching the sampling syringe to the sorbent tube consists of a reducing union (1/4" to 1/16" O.D. -- Swagelok Cat. # SS-400-6-ILV or equivalent) with a 1/4" I.D. silicone O-ring replacing the ferrules in the nut on the 1/4" (sorbent tube) side and the needle of a luer-lock syringe needle inserted into the 1/16" side. (Held in place with a 1/16" ferrule.) The luer-lock end of the needle can be attached to the sampling syringe. It is useful to have a luer-lock on/off valve situated between the syringe and the needle.

C. Two-stage glass sampling cartridge (1/4" O.D. x 1/8" I.D. x 5 1/8") contained in a flame-sealed tube (Manufacturer: Supelco Custom Tenax/Spherocarb Tubes) containing two sorbent sections retained by glass wool:

Front section: 150 mg of Tenax-GC
Back section: 150 mg of CMS (Carbonized Molecular Sieve)

These tubes are prepared and cleaned in accordance with EPA Method EMSL/RTP-SOP-EMD-013 by the vendor. The vendor sends ten tubes per lot made to the REAC GC/MS Laboratory and they are tested for cleanliness, precision, and reproductability.

D. Teflon-capped culture tubes or stainless steel tube containers for sorbent tube storage and shipping. These containers should be conditioned by baking at 120 degrees C for at least two hours. The culture tubes should contain a glass wool plug to prevent sorbent tube breakage during transport. Reconditioning of the containers should occur between uses or after extended periods of disuse (i.e., two weeks or more).

E. Nylon gloves or lint-free cloth. (Hewlett Packard Part # 8650-0030 or equivalent.)

### 7.4.2 Sample Collection

Handle sorbent tubes with care, using nylon gloves (or other lint-free material) to avoid contamination.

Immediately before sampling, break one end of the sealed tube and remove the Tenax cartridge.

Connect the valve on the Tedlar bag to the sorbent tube adapter. Connect the sorbent tube to the sorbent tube adapter with the Tenax (white granular) side of the tube facing the Tedlar bag. Connect the sampling syringe assembly to the CMS (black) side of the sorbent tube. Fittings on the adapters should be finer-tight. Open the valve on the Tedlar bag. Open the on/off valve of the sampling syringe. Depending on work plan stipulations, at least 10% of the soil gas samples analyzed by this GC method must be submitted for confirmational GC/MS analysis (according to modified methods TO-1 [Tenax absorbent] and TO-2 [Carbon Molecular Sieve (CMS) absorbent]). Each soil gas sample must be absorbed on replicate Tenax/CMS tubes. The volume absorbed on a Tenax/CMS tube is dependent on the total concentration of the compounds measured by the photovac/GC or other applicable GC:

| Total Concentration (ppm) | Sample Volume (mL) |
|---|---|
| >10 | Use Serial Dilution |
| 10 | 10 - 50 |
| 5 | 20-100 |
| 1 | 100-250 |

After sampling, remove the tube from the sampling train with gloves or a clean cloth. DO NOT LABEL OR WRITE ON THE TENAX/CMS TUBE.

Place the sorbent tube in a conditioned stainless steel tube holder or culture tube. Culture tube caps should be sealed with Teflon tape.

### 7.4.3 Sample Labeling

Each sample tube container (not tube) must be labeled with the site name, sample station number, date sampled, and volume sampled.

Chain of custody sheets must accompany all samples to the laboratory.

### 7.4.4 Quality Assurance (QA)

Before field use, a QA check should be performed on each batch of sorbent tubes by analyzing a tube by thermal desorption/cryogenic trapping GC/MS.

At least one blank sample must be submitted with each set of samples collected at a site. This trip blank must be treated the same as the sample tubes except no sample will be drawn through the tube.

Sample tubes should be stored out of UV light (i.e., sunlight) and kept on ice until analysis. Samples should be taken in duplicate, when possible.

## 7.5 Summa Canister Sampling

1. Follow step 7.2.1 to evacuate well volume. If PID/FID readings were taken prior to taking a sample, evacuation is not necessary.

2. Attach a certified clean, evacuated 6-liter Summa canister via the 1/4" Teflon tubing.

3. Open valve on Summa canister. The soil gas sample is drawn into the canister by pressure equilibration. The approximate sampling time for a 6 liter canister is 20 minutes.

4. Site name, sample location, number, and date must be recorded on a chain of custody form and on a blank tag attached to the canister.

# 8.0 CALCULATIONS

## 8.1 Field Screening Instruments

Instrument readings are usually read directly from the meter. In some cases, the background level at the soil gas station may be subtracted:

Final Reading = Sample Reading - Background

## 8.2 Photovac GC Analysis

Calculations used to determine concentrations of individual components by Photovac GC analysis are beyond the scope of this SOP and are covered in ERT SOP #2109, *Photovac GC Analysis for Soil Water and Air/Soil Gas.*

## 9.0 CALIBRATION

### 9.1 Field Instruments

It is recommended that the manufacturers' manuals be consulted for correct use and calibration of all instrumentation.

### 9.2 Gilian Model HFS113A Air Sampling Pumps

Flow should be set at approximately 3.0 L/min; accurate flow adjustment is not necessary. Pumps should be calibrated prior to bringing into the field.

## 10.0 QUALITY ASSURANCE/ QUALITY CONTROL

### 10.1 Sample Probe Contamination

Sample probe contamination is checked between each sample by drawing ambient air through the probe via a Gilian pump and checking the response of the FID/PID. If readings are higher than background, replacement or decontamination is necessary.

Sample probes may be decontaminated simply by drawing ambient air through the probe until the HNu reading is at background. More persistent contamination can be washed out using methanol and water, then air drying. For persistent volatile contamination, use of a portable propane torch may be needed. Using a pair of pliers to hold the probe, run the torch up and down the length of the sample probe for approximately 1-2 minutes. Let the probe cool before handling. When using this method, make sure to wear gloves to prevent burns. Having more than one probe per sample team will reduce lag times between sample stations while probes are decontaminated.

### 10.2 Sample Train Contamination

The Teflon line forming the sample train from the probe to the Tedlar bag should be changed on a daily basis. If visible contamination (soil or water) is drawn into the sampling train, it should be changed immediately. When sampling in highly contaminated areas, the sampling train should be purged with ambient air, via a Gilian pump, for approximately 30 seconds between each sample. After purging, the sampling train can be checked using an FID or PID, or other field monitoring device, to establish the cleanliness of the Teflon line.

### 10.3 FID/PID Calibration

The FID and PIDs should be calibrated at least once a day using the appropriate calibration gases.

### 10.4 Field Blanks

Each cooler containing samples should also contain one Tedlar bag of ultra-zero grade air, acting as a field blank. The field blank should accompany the samples in the field (while being collected) and when they are delivered for analysis. A fresh blank must be provided to be placed in the empty cooler pending additional sample collection. One new field blank per cooler of samples is required. A chain of custody sheet must accompany each cooler of samples and should include the blank that is dedicated to that group of samples.

### 10.5 Trip Standards

Each cooler containing samples should contain a Tedlar bag of standard gas to calibrate the analytical instruments (Photovac GC, etc.). This trip standard will be used to determine any changes in concentrations of the target compounds during the course of the sampling day (e.g., migration through the sample bag, degradation, or adsorption). A fresh trip standard must be provided and placed in each cooler pending additional sample collection. A chain of custody sheet should accompany each cooler of samples and should include the trip standard that is dedicated to that group of samples.

### 10.6 Tedlar Bag Check

Prior to use, one bag should be removed from each lot (case of 100) of Tedlar bags to be used for sampling and checked for possible contamination as follows: the test bag should be filled with ultra-zero grade air; a sample should be drawn from the bag and analyzed via Photovac GC or whatever method is to be used for sample analysis. This procedure will ensure sample container cleanliness prior to the start of the sampling effort.

## 10.7 Summa Canister Check

From each lot of four cleaned Summa canisters, one is to be removed for a GC/MS certification check. If the canister passes certification, then it is re-evacuated and all four canisters from that lot are available for sampling.

If the chosen canister is contaminated, then the entire lot of four Summas must be recleaned, and a single canister is re-analyzed by GC/MS for certification.

## 10.8 Options

### 10.8.1 Duplicate Samples

A minimum of 5% of all samples should be collected in duplicate (i.e., if a total of 100 samples are to be collected, five samples should be duplicated.) In choosing which samples to duplicate, the following criteria applies: if, after filling the first Tedlar bag, and, evacuating the well for 15 seconds, the second HN (or other field monitoring device being used) reading matches or is close to (within 50%) the first reading, a duplicate sample may be taken.

### 10.8.2 Spikes

A Tedlar bag spike and Tenax tube spike may be desirable in situations where high concentrations of contaminants other than the target compounds are found to exist (landfills, etc.). The additional level of QA/QC attained by this practice can be useful in determining the effects of interferences caused by these non-target compounds. Summa canisters containing samples are not spiked.

# 11.0 DATA VALIDATION

## 11.1 Blanks (Field and Tedlar Bag Check)

For each target compound, the level of concentration found in the sample must be greater than three times the level (for that compound) found in the field blank which accompanied that sample to be considered valid. The same criteria apply to target compounds detected in the Tedlar bag pre-sampling contamination check.

# 12.0 HEALTH AND SAFETY CONSIDERATIONS

Due to the remote nature of sampling soil gas, special considerations can be taken with regard to health and safety. Because the sample is being drawn from underground, and no contamination is introduced into the breathing zone, soil gas sampling usually occurs in Level D. Ambient air is constantly monitored using the HNu PI101 to obtain background readings during the sampling procedure. As long as the levels in ambient air do not rise above background, no upgrade of the level of protection is needed.

When conducting soil gas sampling, leather gloves should be worn, and proper slam bar techniques should be implemented (bend knees). Also, an underground utility search should be performed prior to sampling. (See Section 4.5).

# 13.0 REFERENCES

Gilian Instrument Corp., Instruction Manual for Hi Flow Sampler: HFS113, HFS 113 T, HFS 113U, HFS 113 UT, 1983.

HNu Systems, Inc., Instruction Manual for Model PI 101 Photoionization Analyzer, 1975.

N.J.D.E.P., Field Sampling Procedures Manual, Hazardous Waste Programs, February, 1988.

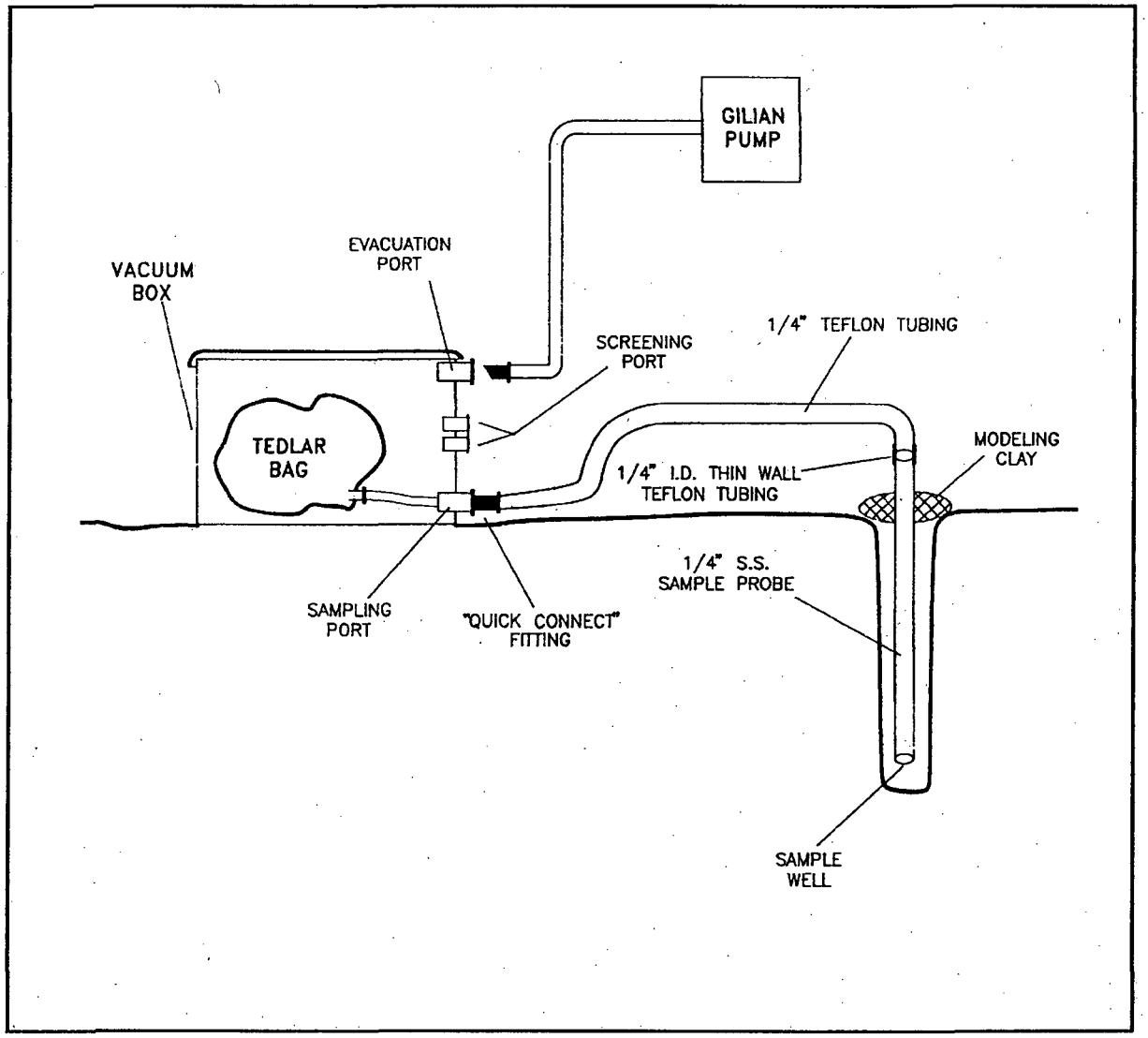
Roy F. Weston, Inc., Weston Instrumentation Manual, Volume I, 1987.

U.S.E.P.A., Characterization of Hazardous Waste Sites - A Methods Manual: Volume II, Available Sampling Methods, 2nd Edition, EPA-600/4-84-076, December, 1984.

# APPENDIX A

Figure

FIGURE 1. Sampling Train Schematic



# APPENDIX B

## HNu Field Protocol

Field Procedure

The following sections detail the procedures that are to be followed when using the HNu in the field.

Startup Procedure

a. Before attaching the probe, check the function switch on the control panel to ensure that it is in the off position. Attach the probe by plugging it into the interface on the top of the readout module. Use care in aligning the prongs in the probe cord with the plug in; don't force.

b. Turn the function switch to the battery check position. The needle on the meter should read within or above the green battery are on the scale. If not, recharge the battery. If the red indicator light comes on, the battery needs recharging.

c. Turn the function switch to any range setting. Look into the end of the probe for no more than two to three seconds to see if the lamp is on. If it is on, it will give a purple glow. Do not stare into the probe any longer than three seconds. Long term exposure to UV light can damage eyes. Also, listen for the hum of the fan motor.

d. To ZERO the instrument, turn the function switch to the standby position and rotate the zero adjustment until the meter reads zero. A calibration gas is not needed since this is an electronic zero adjustment. If the span adjustment setting is changed after the zero is set, the zero should be rechecked and adjusted, if necessary. Wait 15 to 20 seconds to ensure that the zero reading is stable. If necessary, readjust the zero.

Operational Check

a. Follow the startup procedure.

b. With the instrument set on the 0-20 range, hold a solvent-based major market near the probe tip. If the meter deflects upscale, the instrument is working.

Field Calibration Procedure

a. Follow the startup procedure and the operational check.

b. Set the function switch to the range setting for the concentration of the calibration gas.

c. Attach a regulator (HNu 101-351) to a disposable cylinder of isobutylene gas (HNu 101-351). Connect the regulator to the probe of the HNu with a piece of clean Tygon tubing. Turn on the value on the regulator.

d. After fifteen seconds, adjust the span dial until the meter reading equals the concentration of the calibration gas used. Be careful to unlock the span dial before adjusting it. If the span has to be set below 3.0, calibration internally or return to equipment maintenance for repair.

e. Record in the field logbook: the instrument ID no. (EPA decal or serial number if the instrument is a rental); the initial and final span settings; the date and time; concentration and type of calibration has used; and the name of the person who calibrated the instrument.

Operation

a. Follow the startup procedure, operational check, and calibration check.

b. Set the function switch to the appropriate range. If the concentration of gases or vapors is unknown, set the function switch to the 0-20 ppm range. Adjust it if necessary.

c. While taking care not to permit the HNu to be exposed to excessive moisture, dirt, or contamination, monitor the work activity as specified in the Site Health and Safety Plan.

d. When the activity is completed or at the end of the day, carefully clean the outside of the HNu with a damp disposable towel to remove any visible dirt. Return the HNu to a secure area and place on charge.

e. With the exception of the probe's inlet and exhaust, the HNu can be wrapped in clear plastic to prevent it form becoming contaminated and to prevent water from getting inside in the event of precipitation.

# USEPA. 1995. ENVIRONMENTAL RESPONSE TEAM (ERT) STANDARD OPERATING PROCEDURE (SOP) # 1704

# SUMMA CANISTER SAMPLING

SOP#: 1704
DATE: 07/27/95
REV. #: 0.1

## 1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe a procedure for sampling of volatile organic compounds (VOCs) in ambient air. The method is based on samples collected as whole air samples in Summa passivated stainless steel canisters. The VOCs are subsequently separated by gas chromatography (GC) and measured by mass-selective detector or multidetector techniques. This method presents procedures for sampling into canisters at final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. The organic compounds that have been successfully collected in pressurized canisters by this method are listed in the Volatile Organic Compound Data Sheet (Appendix A). These compounds have been measured at the parts per billion by volume (ppbv) level.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

## 2.0 METHOD SUMMARY

Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. Both modes may also use a mass flow controller/vacuum pump arrangement to regulate flow. With the above configuration, a sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated Summa passivated canister. Alternatively, subatmospheric pressure sampling may be performed using a fixed orifice, capillary, or adjustable micrometering valve in lieu of the mass flow controller/vacuum pump arrangement for taking grab samples or short duration time-integrated samples. Usually, the alternative types of flow controllers are appropriate only in situations where screening samples are taken to assess for future sampling activities.

## 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded. Sample holding times and expiration should be determined prior to initiating field activities.

## 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned.

## 5.0 EQUIPMENT/APPARATUS

The following equipment/apparatus (Figure 1, Appendix B) is required:

## 5.1 Subatmospheric Pressure Sampling Equipment

1. VOC canister sampler - whole air sampler capable of filling an initially evacuated canister by action of the flow controlled pump from vacuum to near atmospheric pressure. (Andersen Samplers Inc., Model 87-100 or equivalent).

2. Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

3. Sample canister - leak-free stainless steel pressure vessels of desired volume with valve and Summa passivated interior surfaces (Scientific Instrumentation Specialist, Inc., ID 83843, Andersen Samplers, Inc., or equivalent).

4. Particulate matter filter - 2-µm sintered stainless steel in-line filter (Nupro Co., Model SS-2F-K4-2, or equivalent).

5. Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, Cat. #8125, or equivalent). All materials in contact with sample, analyte, and support gases should be chromatographic grade stainless steel.

6. Fixed orifice, capillary, or adjustable micrometering valve - used in lieu of the electronic flow controller/vacuum pump for grab samples or short duration time-integrated samples.

## 5.2 Pressurized Sampling Equipment

1. VOC canister sampler - whole air sampler capable of filling an initially evacuated canister by action of the flow controlled pump from vacuum to near atmospheric pressure. (Andersen Samplers Inc., Model 87-100).

2. Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

3. Sample canister - leak-free stainless steel pressure vessels of desired volume with valve and Summa passivated interior surfaces (Scientific Instrumentation Specialist, Inc., ID 83843, Andersen Samplers, Inc., or equivalent).

4. Particulate matter filter - 2-µm sintered stainless steel in-line filter (Nupro Co., Model SS-2F-K4-2, or equivalent).

5. Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, Cat. #8125, or equivalent). All materials in contact with sample, analyte, and support gases should be chromatographic grade stainless steel.

# 6.0 REAGENTS

This section is not applicable to this SOP.

# 7.0 PROCEDURE

## 7.1 Subatmospheric Pressure Sampling

### 7.1.1 Sampling Using a Fixed Orifice, Capillary, or Adjustable Micrometering Valve

1. Prior to sample collection, the appropriate information is completed on the Canister Sampling Field Data Sheet (Appendix C).

2. A canister, which is evacuated to 0.05 mm Hg and fitted with a flow restricting device, is opened to the atmosphere containing the VOCs to be sampled.

3. The pressure differential causes the sample to flow into the canister.

4. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-integrated samples (duration of 12 to 24 hours). The sampling duration depends on the degree to which the flow is restricted.

5. A critical orifice flow restrictor will have a decrease in the flow rate as the pressure approaches atmospheric.

6. Upon sample completion at the location, the appropriate information is recorded on the

Canister Sampling Field Data Sheet.

### 7.1.2 Sampling Using a Mass Flow Controller/Vacuum Pump Arrangement (Andersen Sampler Model 87-100)

1. Prior to sample collection the appropriate information is completed on the Canister Sampling Field Data Sheet (Appendix C).

2. A canister, which is evacuated to 0.05 mm Hg and connected in line with the sampler, is opened to the atmosphere containing the VOCs to be sampled.

3. A whole air sample is drawn into the system through a stainless steel inlet tube by a direct drive blower motor assembly.

4. A small portion of this whole air sample is pulled from the inlet tube by a specially modified inert vacuum pump in conjunction with a mass flow controller.

5. The initially evacuated canister is filled by action of the flow controlled pump to near atmospheric pressure.

6. A digital time-program is used to pre-select sample duration and start and stop times.

7. Upon sample completion at the location, the appropriate information is recorded on the Canister Sampling Field Data Sheet.

## 7.2 Pressurized Sampling

### 7.2.1 Sampling Using a Mass Flow Controller/Vacuum Pump Arrangement (Anderson Sampler Model 87-100)

1. Prior to sample commencement at the location, the appropriate information is completed on the Canister Sampling Field Data Sheet.

2. A canister, which is evacuated to 0.05 mm Hg and connected in line with the sampler, is opened to the atmosphere containing the VOCs to be sampled.

3. A whole air sample is drawn into the system through a stainless steel inlet tube by a direct drive blower motor assembly.

4. A small portion of this whole air sample is pulled from the inlet tube by a specially modified inert vacuum pump in conjunction with a mass flow controller.

5. The initially evacuated canister is filled by action of the flow controlled pump to a positive pressure not to exceed 25 psig.

6. A digital time-programmer is used to pre-select sample duration and start and stop times.

7. Upon sample completion at the location, the appropriate information is recorded on the Canister Sampling Field Data Sheet.

## 8.0 CALCULATIONS

1. A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling over the desired sample period. The flow rate can be calculated by:

$$F = \frac{(P)(V)}{(T)(60)}$$

where:

| | | |
|---|---|---|
| F | = | flow rate ($cm^3$/min) |
| P | = | final canister pressure, atmospheres absolute |
| V | = | volume of the canister ($cm^3$) |
| T | = | sample period (hours) |

For example, if a 6-L canister is to be filled to 202 kPa (two atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{(2)(6000)}{(24)(60)} = 8.3 cm^3/min$$

2. If the canister pressure is increased, a dilution factor (DF) is calculated and recorded on the sampling data sheet.

$$DF = \frac{Ya}{Xa}$$

where:

Xa = canister pressure (kPa, psia) absolute before dilution.

Ya = canister pressure (kPa, psia) absolute after dilution.

After sample analysis, detected VOC concentrations are multiplied by the dilution factor to determine concentration in the sampled air.

## 9.0 QUALITY ASSURANCE/ QUALITY CONTROL

The following general quality assurance procedures apply:

1. All data must be documented on standard chain of custody records, field data sheets, or site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

## 10.0 DATA VALIDATION

This section is not applicable to this SOP.

## 11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety practices. Specifically, pressurizing of Summa canisters should be performed in a well ventilated room, or preferably under a fume hood. Care must be taken not to exceed 40 psi in the canisters. Canisters are under pressure, albeit only 20-30 psi, and should not be dented or punctured. They should be stored in a cool dry place and always be placed in their plastic shipping boxes during transport and storage.

## 12.0 REFERENCES


1. Ralph M. Riggin, Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, EPA-600/4-83-027 U. S. Environmental Protection Agency, Research Triangle Park, NC, 1983.

2. W. A. McClenny, J. D. Pleil, T. A. Lumpkin and K. D. Oliver, "Update on Canister-Based Samplers for VOCs," Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, May, 1987 APCA Publication VIP-8, EPA 600/9-87-010.

3. J. F. Walling, "The Utility of Distributed Air Volume Sets When Sampling Ambient Air Using Solid Adsorbents," Atmospheric Environ., 18:855-859, 1984.

4. J. F. Walling, J. E. Bumgarner, J. D. Driscoll,C. M. Morris, A. E. Riley, and L. H. Wright, "Apparent Reaction Products Desorbed From Tenax Used to Sample Ambient Air," Atmospheric Environ., 20:51-57, 1986.

5. Portable Instruments User's Manual for Monitoring VOC Sources, EPA-340/1-88-015, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Washington, D.C., June 1986.

6. R. A. Rasmussen and J. E. Lovelock, Atmospheric Measurements Using Canister Technology, J. Geophys. Res., 83: 8369-8378, 1983.

7. R. A. Rasmussen and M. A. K. Khalil, "Atmospheric Halocarbon: Measurements and Analysis of Selected Trace Gases," Proc. NATO ASI on Atmospheric Ozone, BO: 209-231.

8. EPA Method TO-14 "Determination of Volatile Organic Compounds (VOC's) in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analysis", May 1988.

# APPENDIX A

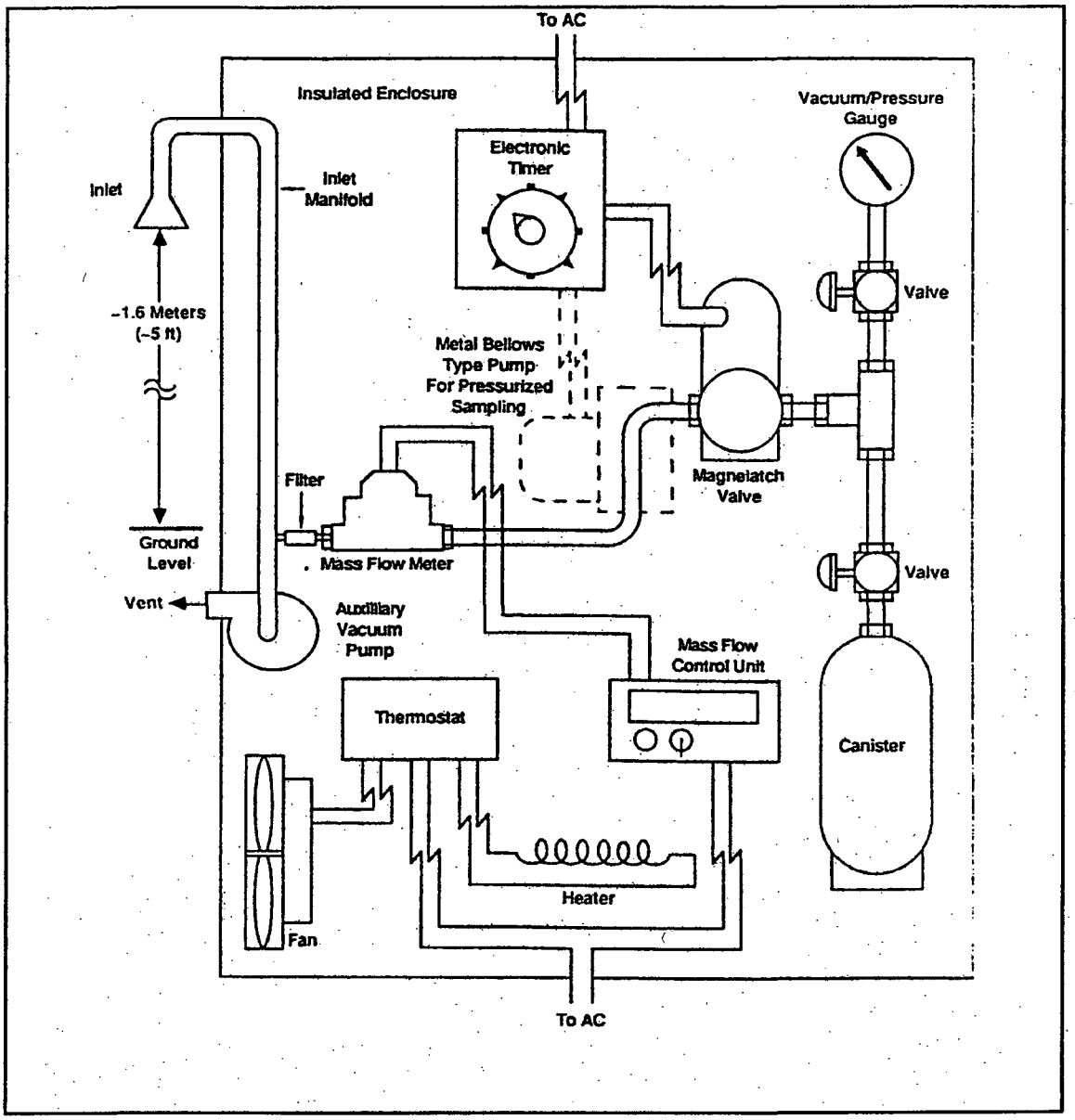
## Volatile Organic Compound Data Sheet

TABLE 1. VOLATILE ORGANIC COMPOUND DATA SHEET

| COMPOUND (SYNONYM) | FORMULA | MOLECULAR WEIGHT | BOILING POINT (°C) | MELTING POINT (°C) | CAS NUMBER |
|---|---|---|---|---|---|
| Freon 12 (Dichlorodifluoromethane) | $Cl_2CF_2$ | 120.91 | -29.8 | -158.0 | |
| Methyl chloride (Chloromethane) | $CH_3Cl$ | 50.49 | -24.2 | -97.1 | 74-87-3 |
| Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane) | $ClCF_2CClF_2$ | 170.93 | 4.1 | -94.0 | |
| Vinyl chloride (Chloroethylene) | $CH_2=CHCl$ | 62.50 | -13.4 | -1538.0 | 75-01-4 |
| Methyl bromide (Bromomethane) | $CH_3Br$ | 94.94 | 3.6 | -93.6 | 74-83-9 |
| Ethyl chloride (Chloroethane) | $CH_3CH_2Cl$ | 64.52 | 12.3 | -136.4 | 75-00-3 |
| Freon 11 (Trichlorofluoromethane) | $CCl_3F$ | 137.38 | 23.7 | -111.0 | |
| Vinylidene chloride (1,1-Dichloroethene) | $C_2H_2Cl_2$ | 96.95 | 31.7 | -122.5 | 75-35-4 |
| Dichloromethane (Methylene chloride) | $CH_2Cl_2$ | 84.94 | 39.8 | -95.1 | 75-09-2 |
| Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane) | $CF_2ClCCl_2F$ | 187.38 | 47.7 | -36.4 | |
| 1,1-Dichloroethane (Ethylidene chloride) | $CH_3CHCl_2$ | 98.96 | 57.3 | -97.0 | 74-34-3 |
| cis-1,2-Dichloroethylene | $CHCl=CHCl$ | 96.94 | 60.3 | -80.5 | |
| Chloroform (Trichloromethane) | $CHCl_3$ | 119.38 | 61.7 | -63.5 | 67-66-3 |
| 1,2-Dichloroethane (Ethylene dichloride) | $ClCH_2CH_2Cl$ | 98.96 | 83.5 | -35.3 | 107-06-2 |
| Methyl chloroform (1,1,1-Trichloroethane) | $CH_3CCl_3$ | 133.41 | 74.1 | -30.4 | 71-55-6 |
| Benzene (Cyclohexatriene) | $C_6H_6$ | 78.12 | 80.1 | 5.5 | 71-43-2 |
| Carbon tetrachloride (Tetrachloromethane) | $CCl_4$ | 153.82 | 76.5 | -23.0 | 56-23-5 |
| 1,2-Dichloropropane (Propylene dichloride) | $CH_3CHClCH_2Cl$ | 112.99 | 96.4 | -100.4 | 78-87-5 |
| Trichloroethylene (Trichloroethene) | $ClCH=CCl_2$ | 131.29 | 87 | -73.0 | 79-01-6 |
| cis-1,3-Dichloropropene (cis-1,3-dichloropropylene) | $CH_3CCl=CHCl$ | 110.97 | 76 | | |
| trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene) | $ClCH_2CH=CHCl$ | 110.97 | 112.0 | | |
| 1,1,2-Trichloroethane (Vinyl trichloride) | $CH_2ClCHCl_2$ | 133.41 | 113.8 | -36.5 | 79-00-5 |
| Toluene (Methyl benzene) | $C_6H_5CH_3$ | 92.15 | 110.6 | -95.0 | 108-88-3 |
| *1,2-Dibromoethane (Ethylene dibromide)* | $BrCH_2CH_2Br$ | 187.88 | 131.3 | 9.8 | 106-93-4 |
| Tetrachloroethylene (Perchloroethylene) | $Cl_2C=CCl_2$ | 165.83 | 121.1 | -19.0 | 127-18-4 |
| Chlorobenzene (Phenyl chloride) | $C_6H_5Cl$ | 112.56 | 132.0 | -45.6 | 108-90-7 |
| *Ethylbenzene* | $C_6H_5C_2H_5$ | 106.17 | 136.2 | -95.0 | 100-41-4 |
| m-Xylene (1,3-Dimethylbenzene) | $1,3-(CH_3)_2C_6H_4$ | 106.17 | 139.1 | -47.9 | |
| p-Xylene (1,4-Dimethylxylene) | $1,4-(CH_3)_2C_6H_4$ | 106.17 | 138.3 | 13.3 | |
| Styrene (Vinyl benzene) | $C_6H_5CH=CH_2$ | 104.16 | 145.2 | -30.6 | 100-42-5 |
| 1,1,2,2-Tetrachloroethane | $CHCl_2CHCl_2$ | 167.85 | 146.2 | -36.0 | 79-34-5 |
| o-Xylene (1,2-Dimethylbenzene) | $1,2-(CH_3)_2C_6H_4$ | 106.17 | 144.4 | -25.2 | |
| 1,3,5-Trimethylbenzene (Mesitylene) | $1,3,5-(CH_3)_3C_6H_6$ | 120.20 | 164.7 | -44.7 | 108-67-8 |
| 1,2,4-Trimethylbenzene (Pseudocumene) | $1,2,4-(CH_3)_3C_6H_6$ | 120.20 | 169.3 | -43.8 | 95-63-6 |
| m-Dichlorobenzene (1,3-Dichlorobenzene) | $1,3-Cl_2C_6H_4$ | 147.01 | 173.0 | -24.7 | 541-73-1 |
| Benzyl chloride (α-Chlorotoluene) | $C_6H_5CH_2Cl$ | 126.59 | 179.3 | -39.0 | 100-44-7 |
| o-Dichlorobenzene (1,2-Dichlorobenzene) | $1,2-Cl_2C_6H_4$ | 147.01 | 180.5 | -17.0 | 95-50-1 |
| p-Dichlorobenzene (1,4-Dichlorobenzene) | $1,4-Cl_2C_6H_4$ | 147.01 | 174.0 | 53.1 | 106-46-7 |
| 1,2,4-Trichlorobenzene | $1,2,4-Cl_3C_6H_3$ | 181.45 | 213.5 | 17.0 | 120-82-1 |
| Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene) | | | | | |

# APPENDIX B

FIGURE 1. Subatmospheric/Pressurized Sampling Equipment



# APPENDIX C

Canister Sampling Field Data Sheet

Page ___ of ___

SUMMA AIR SAMPLING WORK SHEET

Site: _____ Site#: _____
Samplers: _____ Work Assignment Manager: _____
Date: _____ Project Leader: _____

| | | | | | |
|---|---|---|---|---|---|
| Sample # | | | | | |
| Location | | | | | |
| SUMMA ID | | | | | |
| Orifice Used | | | | | |
| Analysis/Method | | | | | |
| Time (Start) | | | | | |
| Time (Stop) | | | | | |
| Total Time | | | | | |
| SUMMA WENT TO AMBIENT | YES/NO | YES/NO | YES/NO | YES/NO | YES/NO |
| Pressure Gauge | | | | | |
| Pressure Gauge | | | | | |
| Flow Rate (Pre) | | | | | |
| Flow Rate (Post) | | | | | |
| Flow Rate (Average) | | | | | |
| MET Station On-site? Y / N | | | | | |
| General Comments: | | | | | |

# SENTINAL MOBILE LABORATORY SOP

SENTINEL MOBILE LABORATORIES

## SENTINEL MOBILE LABORATORIES, LLC – STANDARD OPERATING PROCEDURES (SOPs)

**HAPSITE METHOD OVERVIEW No. 3.0:**

**HAPSITE GCMS METHOD FOR VOLATILE ORGANIC COMPOUNDS IN SOIL VAPOR SAMPLED VIA TEDLAR BAG.**

### 1.0 Introduction

The INFICON HAPSITE FIELD-PORTABLE GCMS is used to determine volatile organic compounds in soil vapor. The method is applicable to a wide range of organic compounds that are volatile enough to be airborne under "normal" atmospheric and temperature conditions. The method is appropriate for analysis of a range of compounds equivalent to those listed within USEPA 8260B.

### 2.0 Instrumentation

INFICON HAPSITE Field-Portable Gas Chromatograph – Mass Spectrometer (GC-MS)
Sample introduction via direct sampling from Tedlar bag by internal sampling pump and integrated heated transfer line.
Carrier gas = Nitrogen
Data System = Integral Intel Pentium processor and external Windows based laptop.
Built in National Institute of Standards and Technology (NIST) and AMDIS Mass Spectral Libraries.
Mass Spectrometer mass range = 1-300 AMU
Detector = Electron Multiplier
Vacuum System = Non evaporable getter pump (NEG pump)
GC column = 30m x 0.32 mm id.

### 3.0 MDLs

The method is capable of producing target compound minimum detection levels of 1.0 ug/m3 or lower.

**4.0 Method Summary**

The method utilizes an Inficon Hapsite propriatory-configured sampling and analysis GCMS system that, through calibration, via volatilized standards of known concentrations in tedlar bags and absorbtion onto a multi-phase trap and subsequent desorption of target compounds, column chromatographic separation of target compounds, fragmentation into ions and mass spectral matching, allows identification and concentration valuation of soil vapor samples.

Note that samples drawn into the sampling system from the Tedlar bag are automatically spiked with internal standards such that an internal standard calibration can be utilized for quantification.

**5.0 Quality control**

The instrument is calibrated for target compounds utilizing a five point calibration (HAPSITE defined as a "Linear curve fit through origin"). The calibration range is from 0.5 ug/m3 to 100.0 ug/m3. The initial calibration curves usually have a deviation of between 5.0 and 15%.

The performance of the mass spectrometer (tuning) is verified at the beginning of every day and at the end of every 12 hour period.

Blanks (ambient air or instrument blanks as appropriate), calibration verification samples (+ or – 20% acceptibility criteria) and lab control samples are run with each batch of unknown samples (dependant on any pre-defined project data quality objectives).

END.

# EXAMPLE QUESTIONNAIRE

# INDOOR AIR QUALITY BUILDING CHARACTERISTIC SURVEY

Occupant/Building Name:_____ Date: _____

Address: _____

Telephone No. Home_____Work _____Best time to contact_____

Completed by:_____

canister# _____ Time Started:_____ Time Stopped:_____
location:_____
canister# _____ Time Started:_____ Time Stopped:_____
location:_____
canister# _____ Time Started:_____ Time Stopped:_____
location:_____
canister# _____ Time Started:_____ Time Stopped:_____
location: _____

Daily Weather Conditions: Temperature_____ Relative Humidity _____

Are you the ❑Owner, ❑Renter, ❑Other (please specify) _____ of this Home/Structure?

Total number of occupants/persons at this location?____ , Children under age 13____ , Children age 13-18____

How long have you lived at this location?_____

Do you regularly use air fresheners?

Do you regularly use or work in a dry cleaning service (check only one box): ❑Yes, use dry cleaning regularly (at least weekly, ❑Yes, use dry-cleaning infrequently (monthly or less)? If yes, when was the lasts time you brought your dry cleaned clothes? _____ ❑Yes, work at a dry cleaning service, ❑No

Does anyone in your home use solvents at work? ❑Yes, ❑ No. If yes, are the work clothes washed at home? ❑Yes ❑No

What is the source of your drinking water? ❑Public water supply, ❑Private well, ❑Other_____

Do you have a private well for purposes other than drinking? ❑Yes, ❑No

Do you have a septic system? ❑Yes, ❑No, ❑Not used, ❑Unknown
Do you have standing water outside your home (pond, ditch, swale)? ❑Yes, ❑No

Where is the washer/dryer located? ❑Basement, ❑Upstairs utility room, ❑Garage, ❑Other_____

Do you have air conditioning? Yes❑ No❑. If yes, please check the appropriate type(s) ❑Central air conditioning, Window air conditioning unit(s), ❑Other ❑, please specify _____

Do you use any of the following? Room fans ❑, Ceiling fans ❑, Attic fan ❑

Water Heater Type: ❑Gas, ❑Electric, ❑Other_____

Water heater location: ❑Basement, ❑Upstairs utility room, ❑Garage, ❑Other_____

What type of cooking appliance do you have? ❑Electric, ❑Gas, ❑Other _____

Type of Home/Structure (check only one): ❑Single Family Home, ❑Duplex, ❑Condominium, ❑Townhouse, ❑Office, ❑commercial, ❑industrial, ❑Other _____

Number of floors below grade:_____, at or above grade: _____

Does this structure have a ❑Basement, ❑Crawlspace or Slab?

Basement/Crawlspace size:_____ft3

Number of rooms in the base: _____

| **OUTSIDE SOURCES** | **YES** | **NO** | **Comments/Locations** |
|---|---|---|---|
| Garbage dumpsters | | | |
| Heavy motor vehicle traffic | | | |
| Construction activities | | | |
| Nearby industries (identify) | | | |
| UST/AST (gasoline, heating fuel) | | | |
| **BASEMENT SURVEY** | | | |
| Wall construction (cinder block, poured concrete, sheet rock, paneling, etc.) | | | type:<br>condition:: |
| Number of windows present on each wall and size | | | North:<br>East:<br>South:<br>West: |
| The basement painted recently?<br>Oil-base or latex paints | | | date:<br>type of paint: |
| The basement ❑finished ❑or unfinished? If finished, how many rooms are in the basement? _____ | | | |
| Does the basement have any of the following? (check all that apply) ❑, Sump ❑, Floor drain ❑, Other hole/opening in floor ❑ (describe) _____ | | | **Notes:** |
| Describe the location of any above appurtenances: | | | **Notes:** |

| OUTSIDE SOURCES | YES | NO | Comments/Locations |
|---|---|---|---|
| Do pipes connect to the sump? (French drain?) | | | |
| New flooring in basement? (list type – carpet, tile) | | | |
| Has glue been used for construction or hobbies? | | | |
| New furniture added to basement | | | type:<br>date: |
| Staining on floors/walls | | | |
| Moisture visually present in the basement | | | |
| Pipes running through walls, floor conduits-describe, give FID/PID/CGS readings) | | | |
| Odors detected by inspector | | | |
| Basement used as living space | | | |
| Time occupants spend in basement (hours/day/per person) | | | |
| Items stored in basement: | **YES** | **NO** | |
| solvents | | | |
| gasoline | | | |
| paint/thinners | | | |
| polishes/waxes | | | |
| insecticides | | | |
| kerosene | | | |
| household cleaning products | | | |
| mothballs | | | |
| other items? | | | |

**NOTES:** _____

_____

_____

**FIRST FLOOR SURVEY**

| | | | |
|---|---|---|---|
| Wall construction binder block, sheet rock, paneling, etc.) | | | type:<br>condition: |
| Was painting done recently?<br>Oil-base or latex? | | | date:<br>type of paint: |
| New flooring on 1st floor?<br>(list type - carpet, tile) | | | |
| Has glue been used for construction or hobbies? | | | |
| New furniture added to 1st floor?<br>(list type – carpet, tile) | | | type:<br>date: |
| Staining on floors/walls | | | |
| Pipes running through walls, floor (describe) | | | |
| Odors detected by inspector | | | |
| | | | |

| OUTSIDE SOURCES | YES | NO | Comments/Locations |
|---|---|---|---|
| Items stored on this floor | | | |
| solvents | | | |
| gasoline | | | |
| paint/thinners | | | |
| polishes/waxes | | | |
| insecticides | | | |
| kerosene | | | |
| household cleaning products | | | |
| mothballs | | | |
| other items? | | | |
| **NOTES:** | | | |
| **PERSONAL ACTIVITIES** | | | |
| Does anyone in the building smoke? | | | |
| Approx. number of tobacco products a day, per person | | | |
| List hobbies of Residents | | | |
| How house pets? | | | |
| **MISCELLANEOUS** | | | |
| Have the occupants ever noticed unusual odors inside or outside the building? | | | |
| Known spill outside or inside building (Specify location) | | | |
| **Type of heating used in building**<br>Oil – (identify the location and age of the storage tank) | | | |
| natural gas | | | |
| electric | | | |
| other (specify) | | | |
| Is the heating unit property vented? | | | |
| Water damage or standing water in building (historic or current) | | | |
| Fire damage to building | | | date: |
| Pest control applications | | | date: |
| | | | |

| OUTSIDE SOURCES | YES | NO | Comments/Locations | | |
|---|---|---|---|---|---|
| FIELD SCREENING RESULTS | FID | PID | CGI | CO2 | Rel. Hum |
| Basement | | | | | |
| First Floor | | | | | |
| Additional Floor | | | | | |
| Other (specify) _____ | | | | | |
| NOTES: | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |

NOTES: _____

02-TBD:PRIN_WP\22864v1.DOC

# EXAMPLE CANISTER FIELD DATA SHEET

# METHOD TO-15 CANISTER SAMPLING FIELD TEST DATA SHEET

## A. GENERAL INFORMATION

Site Location: _____

Site Address: _____

Field ID No: _____ Size of Canister: _____

Sampling Date(s): _____ Canister Serial No: _____

Shipping Date: _____ Flow Controller No: _____

## B. SAMPLING INFORMATION

*TEMPERATURE (Fahrenheit)*

| | Interior | Ambient | Maximum | Minimum |
|---|---|---|---|---|
| Start | | | | |
| Stop | | | | |

*PRESSURE (inches of Hg)*

| | Ambient | Maximum | Minimum |
|---|---|---|---|
| Start | | | |
| Stop | | | |

*CANISTER PRESSURE (inches of Hg) FROM GAUGE*

| | | |
|---|---|---|
| Start | | |
| Stop | | |

*SAMPLING TIMES (24 hour clock)*

| | Local Times | Elapsed Time Meter Reading |
|---|---|---|
| Start | | |
| Stop | | |

_____

Signature/Title of Investigator

## C. LABORATORY INFORMATION

*FLOW RATES (ml/min)*

| | Flow Controller Readout | |
|---|---|---|
| Shipping out from Lab | | required (from lab record log) after return |
| Receiving in Lab | | (if applicable) |

*CANISTER PRESSURE*

| | Inches of Hg | |
|---|---|---|
| Initial Pressure (to field) | | required (from lab record log) after return |
| Final Pressure (from field) | | required (from lab record log) after return |

Data Shipped: _____

Date Received: _____

Individual Canister Certification (provide File #): _____

Batch Certification (provide Batch ID#): _____

_____

Signature/Title
GC/MS Analyst for TO-15

# EXAMPLE CHAIN OF CUSTODY RECORD

STL Burlington
2 South Park Drive
Suite 1
Colchester, VT 05446
phone 802-655-1203 fax 802-655-1248

# Canister Samples Chain of Custody Record

SEVERN TRENT STL

*Severn Trent Laboratories, Inc. (STL) assumes no liability with respect to the collection and shipment of these samples.*

| Client Contact Information | Project Manager: | | of COCs |
|---|---|---|---|
| Company: | Phone: | | |
| Address: | Site Contact: | | |
| City/State/Zip | STL Contact: | | |
| Phone: | | | |
| FAX: | | | |
| Project Name: | Analysis Turnaround Time | | |
| Site: | Standard (Specify) | | |
| PO # | Rush (Specify) | | |

| Sample Identification | Sample Date(s) | Time Start | Time Stop | Canister Vacuum In Field, "Hg (Start) | Canister Vacuum In Field, "Hg (Stop) | Flow Controller ID | Canister ID | TO-15 | TO-14A | EPA 3C | EPA 25C | ASTM D-1946 | Other (Please specify in notes section) | Sample Matrix | Indoor Air | Ambient Air | Soil Gas | Landfill Gas | Other (Please specify in notes section) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | |

| | Temperature (Fahrenheit) | | |
|---|---|---|---|
| | Interior | Ambient | |
| Start | | | |
| Stop | | | |

| | Pressure (inches of Hg) | | |
|---|---|---|---|
| | Interior | Ambient | |
| Start | | | |
| Stop | | | |

**Special Instructions/QC Requirements & Comments:**

| | | | |
|---|---|---|---|
| Canisters Shipped by: | Date/Time: | Canisters Received by: | |
| Samples Relinquished by: | Date/Time: | Received by: | |
| Relinquished by: | Date/Time: | Received by: | |

Lab Use Only Shipper Name: Cleaned/Certified Initials:

# EXAMPLE ACCESS AGREEMENT

## CONSENT TO ACCESS

The purpose of this Consent to Access is for the U.S. Environmental Protection Agency (EPA) to secure access to this property.

By executing this Consent to Access, I hereby consent to and authorize employees, authorized agents, contractors and subcontractors of EPA to enter onto and move about all areas of the property. I understand that the work that will be performed at the property may include the following activities: 1) collection and analysis of exterior soil gas samples from the property, 2) collection and analysis of indoor air samples collected over a 24-hour period, 3) assessment and inventorying of containers and their contents as necessary to determine the potential impact to the air, and 4) assessment and inventorying of the residential structure.

This written permission is given by me voluntarily with knowledge of my right to refuse and without threats or promises of any kind.

I, the undersigned, am authorized to represent the owner of the property.

_____ _____

Signature Date

_____

Name of Property Owner

_____ _____

Name of Authorized Official (Please Print) Title (Please Print)

_____

Address of Property in Which Interest Lies

# RESIDENT INSTRUCTIONS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION II

---

The United States Environmental Protection Agency (EPA) is conducting an investigation of indoor air quality in and around residential homes in your area. Concerns over contamination in the ground and ground water; allegedly linked to an industrial site in the vicinity, has initiated this action. As a result, a consultant on behalf of EPA is collecting indoor air samples from residences in the vicinity of the site.

---

## INDOOR AIR SAMPLING

*Why is the United States Environmental Protection Agency collecting air samples from my basement?*

To determine if contamination in the ground is affecting homes, EPA is testing indoor air quality. As a result, EPA personnel will collect a sample of the air from your basement and analyze it at no charge to you. The sampling event is to determine whether you and/or your family are at risk of breathing harmful contaminants that may be associated with subsurface contamination.

*How is the air being collected from my basement?*

A device, known as a Summa Canister, will be placed in your basement to draw in air for a period of 24 hours. Initially, the summa canister is under a vacuum. The summa canister will be opened in your basement and air will flow into the canister for 24 hours. Air will not flow out of the device. These canisters are completely safe and pose no danger to you or your children.

***What should I <u>NOT DO</u> so that I do not damage or disrupt the summa canister and provide the proper environment for the sampling event?***

**Summa canisters are particularly sensitive, and can be damaged very easily. This is why it is important to practice the following precautions at least 24 hours prior to sampling:**

**-do not smoke in the basement or house**
**-do not open the basement door**
**-do not bring dry-cleaning into the house**
**-do not use solvents of any type**
**-do not open your basement windows**
**-do not utilize fans or vents in the basement**
**-do not paint or clean paint brushes**
**-do not polish your shoes**

**-do not pour gasoline, liquid fuels or solvent inside your house or attached garage**
**-do not park your car inside your attached garage**
**-do not start internal combustion equipment inside your house or attached garage -**
**-do not run the clothes washer or dryer if in the basement**
**-do not move the canister(s) under any circumstances.**

*Who is doing the analysis of the samples?*

Although EPA personnel will be providing oversight of the work conducted on your premises, EPA contractors will be collecting the air samples and a private laboratory has been contracted to perform the analytical procedures.

EPA apologizes for any inconveniences that may occur as part of this sampling event. However, your cooperation, and understanding is greatly appreciated. Remember, we are doing this for the protection of your health, as well as the surrounding community's.

Please call ENVIRON at 609-243-9871 with any questions about the sampling itself or any additional questions you may have. Thank you for your help and cooperation.

02-15593A:PRIN_WP\22879v1.DOC